

TECHNICAL REPORT

for

**IMPACTS OF FIRE ECOLOGY RANGE MANAGEMENT (FERM) ON THE FATE AND
TRANSPORT OF ENERGETIC MATERIALS ON TESTING AND TRAINING RANGES**

Contract No. DACA72-02C-0038

Environmental Restoration Program – 1305

Submitted

to

**Strategic Environmental Research and Development Program (SERDP)
901 North Stuart Street, Suite 303
Arlington, VA 22203**



Battelle
The Business of Innovation

**505 King Avenue
Columbus, OH 43201**

**Prepared
by**

INTTEGRATED
SCIENCE &
TECHNOLOGY, INC.

**1349 Old Hwy 41, Suite 225
Marietta, GA 30060**



**Lower College Rd.
Kingston, RI 02881**

April, 2006

Report Documentation Page			Form Approved OMB No. 0704-0188		
Public reporting burden for the collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to a penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.					
1. REPORT DATE 01 APR 2006	2. REPORT TYPE Final	3. DATES COVERED -			
4. TITLE AND SUBTITLE Impacts of Fire Ecology Range Management (FERM) on the Fate and Transport of Energetic Materials on Testing and Training Ranges		5a. CONTRACT NUMBER DACA72-02C-0038			
		5b. GRANT NUMBER			
		5c. PROGRAM ELEMENT NUMBER			
6. AUTHOR(S) Foote, Eric		5d. PROJECT NUMBER ER 1305			
		5e. TASK NUMBER			
		5f. WORK UNIT NUMBER			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Battelle Memorial Institute 505 King Avenue Columbus, OH 43201 Integrated Science & Technology 1349 Old Hwy 41, Suite 225 Marietta, GA 30060 University of Rhode Island Lower College Rd. Kingston, RI 02881		8. PERFORMING ORGANIZATION REPORT NUMBER			
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Strategic Environmental Research & Development Program 901 N Stuart Street, Suite 303 Arlington, VA 22203		10. SPONSOR/MONITOR'S ACRONYM(S) SERDP			
		11. SPONSOR/MONITOR'S REPORT NUMBER(S)			
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution unlimited					
13. SUPPLEMENTARY NOTES The original document contains color images.					
14. ABSTRACT A growing concern exists that the accumulation of unexploded or unconsumed energetic compound residues in soils on military testing and training ranges represents a threat to human health and the environment and that the ultimate fate and transport of these compounds can be influenced by land management practices. One such practice may be prescribed or controlled burning, which is used on military training ranges for a variety of purposes including safety clearance prior to detection and demolition of unexploded ordnance (UXO), wildfire avoidance, and plant and wildlife management.					
15. SUBJECT TERMS					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 86	19a. NAME OF RESPONSIBLE PERSON
a. REPORT unclassified	b. ABSTRACT unclassified	c. THIS PAGE unclassified			

This report was prepared under contract to the Department of Defense Strategic Environmental Research and Development Program (SERDP). The publication of this report does not indicate endorsement by the Department of Defense, nor should the contents be construed as reflecting the official policy or position of the Department of Defense. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the Department of Defense.

The vendors and products, including the equipment, system components, and other materials identified in this report, are primarily for information purposes only. Although Battelle may have used some of these vendors and products in the past, mention in this report does not constitute Battelle's recommendation for using these vendors or products.

ACKNOWLEDGEMENTS

This work was funded by the Strategic Environmental Research and Development Program (SERDP) under Contract # DACA72-02C-0038, as Cleanup Program # 1305 (subsequently, Environmental Restoration Program # 1305). The SERDP Program Manager for ER-1305 was Dr. Robert Holst and subsequently, Dr. Andrea Leeson. Additional funding was provided by the Air Force Center for Environmental Excellence (AFCEE) under Contract # N47408-01-D-8207, Task Order # 36. The AFCEE component of this program was managed by Mr. Don Ficklen and Mr. John Haliscak.

The field work described in this report was hosted by Eglin AFB and without the outstanding support provided by the various staff at Eglin; this work would not have been possible. The authors would like to acknowledge the many staff at Eglin AFB who assisted in the implementation of this field investigation. These individuals include Mr. Doug Davis and Mr. John Sledge who were the initial point-of-contact (POC) for site operations; Mr. Edward O'Connell who ultimately served in this capacity and became the main contact and overall coordinator for the on-site work performed at Eglin; Mr. Thomas Heffernan, Mr. Michael McClure, and Mr. Charles Sprague and the many range safety and explosive ordnance disposal (EOD) personnel for safety and other logistical and operational guidance; and Mr. William Chandler, Ms. Lora Hyatt and Mr. Michael Hunt for range scheduling assistance.

The controlled burn was designed and conducted by staff at Eglin AFB's Natural Resources Branch at Jackson Guard. The authors would like to acknowledge Mr. Rick McWhite, Mr. James Furman, Mr. Dale Thurber, and Mr. Kevin Hiers who were the primary contacts at Jackson Guard who assisted with the coordination of this investigation. Mr. Hiers ultimately designed and directed the controlled burn and assisted with other on-site sampling activities, including plant species identification; additionally the authors are grateful for services provided by Mr Steve Simpson of Heloworks, who piloted the helicopter that was used to ignite the controlled burn.

The authors would like to acknowledge Dr. Tom Jenkins, Dr. Judith Pennington, and Dr. Jeff Davis and others from USACE-ERDC who provided in-kind support for on-site work and training as well as laboratory samples analysis; and Dr. Victor Medina and Dr. Steve Larson who respectively provided the Battelle Team with the test soil that was used during the burn experiments, and provided technical advisory assistance for energetic residual analysis in plant tissues.

The authors wish to extend their gratitude to Dr. James Smith and Mr. Junqi Yue at the University of Rhode Island, Department of Chemistry for their work associated with the bench-scale energetic degradation testing.

The authors wish to acknowledge Mr. Dave Olsen of IST who assisted in the field sampling and preparation in the field for the burn experiments.

Additionally, the authors would like to acknowledge Mr. Travis Davis of Three Rivers R&D, Inc. and his staff for on-site sampling services and field preparatory services for the controlled burn.

Lastly, the authors would like to acknowledge Battelle scientists and field staff- Ms. Melody Graves, Mr. Shane Walton, Mr. Mike Woolfe, Mr. John Linton; Battelle scientists Ms. Terry Nobles and Ms. Antoinette Andonian who provided the lead analytical support for field samples obtained before and after the burn. Ms. Kimberlea Andrews and Mr. Raj Mangaraj of Battelle who conducted the plant processing and energetic analyses for plant material collected during the site characterization effort.

CONTENTS

	<u>Page</u>
ACKNOWLEDGEMENTS	iii
FIGURES	v
TABLES	vi
ABBREVIATIONS AND ACRONYMS	viii
 1.0 PROJECT BACKGROUND	 1
2.0 TECHNICAL OBJECTIVE.....	3
3.0 TECHNICAL APPROACH.....	3
3.1 Site Selection	3
3.2 Laboratory Thermal Decomposition and Migration Testing.....	4
3.2.1 Explosives Decomposition Study	6
3.2.2 Explosives Migration Study	6
3.3 Initial Site Characterization	7
3.3.1 Sample Processing and Analytical Methods.....	10
3.3.2 Quality Assurance and Quality Control.....	11
3.3.2.1 Precision	12
3.3.2.2 Accuracy.....	12
3.4 Field-Scale Prescribed Burn	13
3.4.1 Pre-Burn Site Activities.....	13
3.4.1.1 Test Soil Preparation	13
3.4.1.2 Test Site Layout.....	14
3.4.1.3 Test Area Layout and Test Systems	14
3.4.1.4 Pre-burn Surface-Soil Sampling	18
3.4.1.5 Pine Straw Spreading.....	18
3.4.2 Controlled Burning	19
3.4.3 Post-Burn Site Activities	20
3.4.3.1 Post-Burn Sampling.....	21
3.4.3.2 Retrieval of Thermocouples and Data Loggers	22
3.4.3.3 Migration Column Retrieval.....	22
3.4.3.4 Melting Column Retrieval	22
3.4.3.5 Surface-Runoff Trap Installation and Sampling.....	22
3.4.4 Post-Burn Laboratory Procedures.....	24
3.4.4.1 Migration Column Processing	24
3.4.4.2 Melting Column Processing	24
3.4.4.3 Soil Processing	24
3.4.4.4 Sample Extraction	25
3.4.4.5 Sample Analysis	26
3.4.5 Quality Assurance and Quality Control.....	27
3.4.5.1 Field Quality Assurance	27
3.4.5.2 Laboratory Quality Assurance	27
3.4.6 Field Schedule for the Controlled Burn.....	28
 4.0 RESULTS AND DISCUSSION	 30
4.1 Laboratory Thermal Decomposition Studies.....	30
4.1.1 Preliminary Examination and Test Design (TNT only).....	30
4.1.2 Kinetics.....	33

4.1.3	Decomposition Gases	36
4.1.4	Migration Studies	38
4.2	Initial Site Characterization	42
4.2.1	Soils Concentrations	42
4.2.2	Plant Tissue and Surface Concentrations	42
4.3	Prescribed Burn	48
4.3.1	Burn Observations and Weather Conditions	48
4.3.2	Temperature	50
4.3.3	Explosive Residual Concentrations in Pre- and Post-Burn Surface Soils	54
4.3.4	Test Soil in Dishes and Pans	55
4.3.5	Migration Columns	62
4.3.6	TNT/RDX Melting Columns	63
4.3.7	Energetic Residuals in Surface Water Runoff and Trapped Sediment	64
5.0	CONCLUSIONS	66
5.1	Conclusions Drawn from Laboratory Testing	66
5.2	Conclusions Drawn from the Field Demonstration	66
6.0	RECOMMENDATIONS FOR FUTURE EFFORTS	68
7.0	LESSONS LEARNED DOING FIELD WORK ON AN ACTIVE RANGE	71
8.0	REFERENCES	73

FIGURES

	<u>Page</u>
Figure 3-1	Site Map Showing Eglin AFB and Range C-52-N 4
Figure 3-2.	Study Area at Cat’s Eye, C52-N, Eglin AFB 8
Figure 3-3.	Conceptual Circular Grid and Segment Layout for Surface Soil and Vegetation Sampling at Site 1 and Site 2 9
Figure 3-4.	Burn Perimeter Containing Test Areas at Cat’s Eye, C52-N, Eglin AFB..... 15
Figure 3-5.	Circular Grid and Deployment Layout for Surface Soil Sampling and Test Soil Deployments at Study Areas E-1, E-2, E-3, and E-4 16
Figure 3-6.	Thermocouple and Data Logger Station and Temperature Indicators 16
Figure 3-7.	Photographs of theThermocouple Station, Data Logger, and Temperature Indicator Strips 17
Figure 3-8.	Migration Column Exposed to Fire..... 19
Figure 3-9.	Spreading Pine Straw at Test Area E-2..... 19
Figure 3-10.	Prepared Test Site with Added Pine Straw Showing Locations of Test Areas 20
Figure 3-11.	Fire Ignition at C-52N..... 21
Figure 3-12.	Post-Fire Sampling and Retrieval Activities 21
Figure 3-13.	Surface Runoff Traps 22
Figure 3-14.	Surface Water Trap Installation 23
Figure 3-15.	Soil Processing in the Laboratory Using Ring and Puck Mill Grinder and Compositing Plan 24
Figure 4-1.	Comparison of TNT Arrhenius Plots of Previous and New Data 30
Figure 4-2.	Preliminary Study: TNT Decomposition Neat and in Sandia and 31
Figure 4-3.	Preliminary Study: TNT Decomposition Neat and in Sandia and 32
Figure 4-4.	Preliminary Study: TNT Decomposition in Several Matrices (60 min @ 175°C)..... 32

Figure 4-5.	Arrhenius Plots of TNT Decomposition	34
Figure 4-6.	Arrhenius Plots of RDX Decomposition.....	35
Figure 4-7.	Arrhenius Plots: RDX and TNT Decomposition Neat and in Eglin Soil (with 0.4% Moisture).....	36
Figure 4-8.	Evolution of Decomposition Gases from 10% TNT in Soil at 250°C	37
Figure 4-9.	CO ₂ Production During TNT Decomposition at 250°C.....	38
Figure 4-10.	Experimental Setup and Results for a TNT Migration Experiment.....	39
Figure 4-11.	Fractions of Soil after Heating for 3 Hours at 250°C.....	40
Figure 4-12.	Soil with TNT (10%) Prior to Heating (Time-Zero).....	41
Figure 4-13.	GC/MS Chromatogram of the Top 1-cm of Soil in RDX Migration Study.....	41
Figure 4-14.	Sampling Results at Cat's Eye, C52-N, Eglin AFB.....	43
Figure 4-15.	Post-Burn Photos of Test Systems	49
Figure 4-16.	Weather Conditions During the Burn	50
Figure 4-17.	Temperature Profiles for Each Test Site During the Burn	51
Figure 4-18.	Maximum Temperatures Recorded as a Function of Fuel Loading	52
Figure 4-19.	Averaged Temperature Profiles from the Two Ground-Surface Thermocouples at Each of the Four Test Plots	55
Figure 4-20.	TNT Concentrations in Soil Dishes After the Burn as a Function of Fuel Load and Soil Layer Thickness.....	60
Figure 4-21.	RDX Concentrations in Soil Dishes Following the Burn as a Function of Fuel Load and Soil Layer Thickness	60
Figure 4-22.	TNT and RDX Concentration Reductions as a Function of Fuel Load	61
Figure 4-23.	Significant Rainfall Events Relative to Surface Water Trap Sampling Activities.....	64

TABLES

	<u>Page</u>
Table 3-1.	Extraction-Solvent and Injection Volumes for TNT and RDX Analysis..... 6
Table 3-2.	Plant Tissue Sample Identification for C52-N Characterization..... 11
Table 3-3.	Physical/Chemical Properties of the Test Soil from the Massachusetts Military Reservation..... 14
Table 3-4.	Analytical Parameters for Explosives Analysis 26
Table 3-5.	Field Schedule of Events..... 29
Table 4-1.	Kinetic Results from Heating Neat TNT in Open Versus Sealed Ampoules..... 30
Table 4-2.	TNT Decomposition Rates and Arrhenius Parameters 34
Table 4-3.	RDX Decomposition Rates and Arrhenius Parameters..... 35
Table 4-4.	Cumulative Decomposition Gases from Neat and Soil-Bound Explosives at 250°C 37
Table 4-5.	Summary of TNT Migration Study Results from Heating at 250°C..... 40
Table 4-6.	Summary of RDX Migration Results after Heating at Multiple Temperatures 40
Table 4-7.	Highest Concentrations of Energetic Concentrations Detected in Surface Soils During the Initial Site Characterization 42
Table 4-8.	Results of Concentration of Explosive Compounds in Surface Soil, On Plant Tissue ^(a) , and In Plant Tissue at Site 1 (Target Impact Area), C52-N, Eglin AFB..... 44
Table 4-9.	Results of Concentration of Explosive Compounds in Surface Soil, On Plant Tissue ^(a) , and In Plant Tissue at Site 2 (Target Impact Area), C52-N, Eglin AFB..... 45
Table 4-10.	Results of Concentration of Explosive Compounds in Surface Soil, On Plant Tissue ^(a) , and In Plant Tissue at Site 3 (Plateau Area-South End of Site), C52-N, Eglin AFB 46
Table 4-11.	Results of Concentration of Explosive in Surface Soil at Site 5 (“Wash-Out” Bed), C52-N, Eglin AFB 47

Table 4-12.	Results of Concentration of Explosive in Surface Soil at Site 6 (“Blowhole”) and Water Samples from the South Stream, C52-N, Eglin AFB	47
Table 4-13.	Averaged Temperatures Recorded from Indicators on the Bottom of the Dishes Filled with Test Soil at Varied Thickness	53
Table 4-14.	Results from Surface Soil Samples Prior To- and Following the Controlled Burn at E-1	56
Table 4-15.	Results from Surface Soil Samples Prior To- and Following the Controlled Burn at E-2	57
Table 4-16.	Results from Surface Soil Samples Prior To- and Following the Controlled Burn at E-3	58
Table 4-17.	Results from Surface Soil Samples Prior To- and Following the Controlled Burn at E-4	59
Table 4-18.	Averaged Residual TNT and RDX Concentrations in Test Soil Placed in Pans.....	62
Table 4-19.	Explosives Residual Distribution (mg) and Mass Removal from Migration Column Experiments	62
Table 4-20.	Explosives Residual Distribution (mg) and Mass Removal from Melting Column Experiments	63
Table 4-21.	Results from Surface Water Run Off Traps after Two Sampling Events	65

ABBREVIATIONS AND ACRONYMS

AD	Analytical duplicate
ADNT	Adenotrinitrotoluene
AFB	Air Force Base
AFCEE	Air Force Center for Environmental Excellence
ags	above ground surface
bgs	below ground surface
cm	centimeter
COC	chain-of-custody
CRREL	Cold Region Research Engineering Laboratory
C52-N	active practice and training range C52 North, Eglin AFB, FL
DNB	Dinitrobenzene
DNT	Dinitrotoluene
DoD	Department of Defense
dGPS	differential global positioning system
ECD	electron capture detector
EOD	explosive ordnance disposal
EPA	United States Environmental Protection Agency
ERDC	United States Army Engineer Research and Development Center
FERM	Fire Ecology Range Management
FD	field duplicate
FL	Florida
GC	gas chromatograph
GC/MS	gas chromatograph/mass spectrometer
GPS	global positioning system
HMX	His Majesty's Explosive or high melting explosive (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetracyclooctane); cyclo-tetra methylene tetranitramine
HPLC	high performance liquid chromatography
i.d.	inside diameter
IPR	in-progress review (meeting)
kg	kilogram
K _{ow}	octanol water partitioning coefficient
LC	liquid chromatograph
LD	laboratory duplicate
m	meter
min	minute
mL	milliliter
MMR	Massachusetts Military Reservation

MS	matrix spike
NB	Nitrobenzene
NG	Nitroglycerine
NT	Nitrotoluene
o.d.	outside diameter
PDA	photodiode array
PI	principal investigator
POC	point of contact
PTFE	polytetrafluoroethylene
QA/QC	quality assurance/quality control
RDP	relative percent difference
RDX	Royal Demolition Explosive
RPM	revolutions per minute
RSD	relative standard deviation
SAB	Scientific Advisory Board
SERDP	Strategic Environmental Research and Development Program
TCD	thermal conductivity detector
TNB	Trinitrobenzene
TNT	2,4,6-Trinitrotoluene
URI	University of Rhode Island
USACE	United States Army Corps of Engineers
UV	ultraviolet
UXO	unexploded ordnance
WES	Water Experiment Station

Impacts of Fire Ecology Range Management (FERM) on the Fate and Transport of Energetic Materials on Testing and Training Ranges, SERDP CP-1305

Battelle, Integrated Science and Technology, Inc.

and

The University of Rhodes Island

1.0 PROJECT BACKGROUND

A growing concern exists that the accumulation of unexploded or unconsumed energetic compound residues in soils on military testing and training ranges represents a threat to human health and the environment and that the ultimate fate and transport of these compounds can be influenced by land management practices. One such practice may be prescribed or controlled burning, which is used on military training ranges for a variety of purposes including safety clearance prior to detection and demolition of unexploded ordnance (UXO), wildfire avoidance, and plant and wildlife management.

During testing of explosive devices, unexploded or unconsumed energetic compounds including hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX), and 2,4,6-trinitrotoluene (TNT) frequently remain as residues in the surface soils. These residues eventually may be transported to surface and ground waters and create a health risk. Currently, there is no protocol for routinely removing explosive residues from surface soils. If procedures were instituted to reduce the levels of energetic compounds in surface soils (the source of groundwater contamination), future impacts to groundwater resources could be significantly reduced or eliminated.

Phytoremediation. Plants can have important effects on the fate and distribution of energetic compounds in soils. Plants can take these compounds up in their tissue, they can metabolize the compounds, they can stabilize soils holding the compounds in place, and they can act as a surface for adherence of energetic compounds. Phytoremediation is frequently applied as a plant based remedial technology for cleanup of soils and groundwater contaminated with any number of organic and/or inorganic compounds, including explosives residuals. While specific transformation pathways have yet to be elucidated, the ability of plants to uptake and transform energetic compounds has been well established (Achtnich et al., 1999; Bhadra et al., 1999; Boyle and Shann, 1998; Carrier and Wolfe, 1996; Chekol et al., 2001; Hughes et al., 1997; 1998; Larson et al., 1999; Medina et al., 1997; Pennington, 1998; Schneider et al., 1994; 1995; Vanderford et al., 1997; Wang and Hughes, 2001; Wang et al., 2000; Just and Schnoor, 2004).

Depending on factors such as soil composition, contaminant concentration, plant species, and site conditions, an organic contaminant may be able to pass through the protective barrier of the rhizosphere (that area of the root zone inducing a symbiotic relationship between soil microorganisms and plant roots) and be taken up into the plant. Direct uptake of organic compounds by plants has been shown to be an efficient removal mechanism useful for sites contaminated with moderately hydrophobic compounds. In general, for a compound to be taken up by a plant it must be in contact with the plant roots and be dissolved in the soil water.

Factors which dictate the ability of contaminants to be available to plant roots include polarity, sorption properties, solubility, and hydrophobicity. The octanol-water partitioning coefficient (K_{ow}) of a compound is the primary parameter often used to estimate the uptake potential of a contaminant into a plant. In general, those compounds that exhibit an intermediate $\log K_{ow}$ (0.5 to 4) tend to be good targets

for phytoremediation because they are taken up by the roots and considered xylem mobile and phloem immobile. Those compounds that exhibit a log K_{ow} below this range tend to be quite soluble, and depending on soil parameters, may not be readily absorbed to the roots or dispersed into the plant. Hydrophobic compounds (log K_{ow} ~4) are generally not sufficiently soluble in water or tend to sorb strongly to the roots and are less likely to be translocated to the shoots. All energetics with a known K_{ow} fall into this intermediate range, and generally may be considered candidates for phytoremediation.

Fire Ecology. Fire ecology is the science of using fire to manage vegetation and ecosystems. Fires in target areas are relatively common occurrences due to natural or controlled causes. Dry grass in target areas can ignite as a result of detonations, but standard practice is to quickly suppress these fires. Prescribed or controlled burns in target areas at DoD practice ranges are currently used as a management technique. For example, at Eglin AFB, the Air Force has developed a systematic approach to prescribed burning of ranges to control vegetation. At Noman's Island MA, the Navy burned the entire island to improve access for UXO clearance. At the New Boston AS, the Air Force regularly burns impact areas both for vegetation control and for safe and efficient UXO clearance. Prescribed burning has been utilized at small-arms ranges to prevent fuel accumulation where tracers frequently cause fires.

These fires have the potential to destroy energetic compounds which are either associated with the plants that are burned or are in or on the surface soils which are heated by the burn. To date, no evaluation of fire facilitated explosives residual destruction in soils at ranges has been done. Prescribed burning occurs infrequently and the practice is not optimized for energetics destruction.

FERM. Fire Ecology Range Management (FERM) is the application of fire ecology principals to develop range management techniques that will minimize the problems associated with explosive residues. This may involve scheduling burns to optimize vegetation either for fuel distribution or to encourage species that are more effective energetic accumulators.

FERM combines fire ecology and phytoremediation into an easily implementable and innovative approach for addressing explosives residual contamination on ranges. Combining the technologies controls the migration of explosives compounds in/from surface soils and thermally destroys the residuals before they reach groundwater or are transported from the site during surface runoff events. Explosives residuals in surface soils, taken up and/or transformed in plant tissue, or deposited on the surface of the vegetation exposed to temperatures above the thermal decomposition temperature as the fire passes and the fuel smolders should be effectively destroyed. Explosive compounds including TNT and RDX are unstable at high temperature and are amenable to thermal decomposition (Oxley et. al. 1994a; Oxley et. al., 1995). Temperature measurements during controlled burning have verified that temperatures are reached above the surface and in the fuel, and below ground surface, are high enough to promote thermal destruction of the explosives compounds (Bailey and Anderson, 1980; Ryan and Frandsen, 1991; Hartford and Frandsen, 1992; Valette et. al., 1994; Molina and Llinares, 2001; Brooks, 2002; Kremens et. al., 2003; Massman et. al., 2003; Boring et al., 2004; Hubbard et. al., 2004; Neary, 2004; Smith et. al., 2005).

The majority of heat produced during controlled burning is transmitted upward and temperature above grade can range between 600°C and 1,200°C (Bailey and Anderson, 1980; Kremens et. al., 2003; Hubbard et. al., 2004; Neary, 2004). These temperatures easily exceed the thermal decomposition temperatures for TNT and RDX, suggesting that those compounds in and on plant tissues should rapidly be destroyed. The situation is not the same for explosive residual contaminants at or below the soil surface. Only 8 to 10 percent of the heat generated during controlled burning is directed downward (De Bano et. al., 1977). The extent of soil heating is a function of both the magnitude and the duration of the fire, which in turn is a function of fuel load and the burning conditions (Debano, 1989; Massman et. al., 2003) with duration more important than intensity (Hungerford, 1989; Neary et. al., 1999). Fires with

ground fuels that burn/smolder for longer periods of time such as fallen trees and logs transfer more heat to soil than do fires fueled by fast burning materials such as pine needles, grasses, or thin and dry duff layers. Most actively used ranges would tend to not have mature trees and logs, putting them into the later class of fire.

2.0 TECHNICAL OBJECTIVE

The objective of this project was to determine the impact that prescribed burning had on the fate and transport of residual energetic compounds in surface soils on test and training ranges. This included:

- determining to what degree burning reduced surface and near-surface energetic residuals
- determining if native plant species accumulated energetic compounds in above surface tissue that was then available to burn
- determining the depth to which burning increased the temperature to levels sufficient to thermally decompose energetic residuals
- determining to what extent varied levels of vegetation (fuel load) impacted the destruction of energetic residual concentrations
- evaluating the potential for vapor emissions of energetic compounds and gaseous thermal decomposition byproducts
- determining the impact of burning on energetic residual infiltration into the soil and melting
- and, determining if surface water runoff/sediment transport was a potential transport mechanism for surface residuals.

3.0 TECHNICAL APPROACH

The technical approach for this study consisted of the following activities:

- site selection – location of a range with an in-use target area which could be burned
- laboratory thermal decomposition melting and migration testing
- initial site characterization
- and, field implementation of a controlled burn.

Each of these activities is described below.

3.1 Site Selection

The primary goal of site selection was to identify a DoD facility that was willing to host the FERM demonstration and to find a site on the installation that was active in order to increase the potential for finding freshly distributed energetic material. It also was of interest to locate a site that had a well established prescribed burn program. Additional criteria included the commitment of in-kind services or funds (for the prescribed burn and explosive ordinance disposal [EOD] support), availability of existing site characterization data, and regulatory and logistical cooperation and support.

Eglin AFB was selected as the facility for conducting the FERM demonstration based on their meeting all of the above criteria. Eglin's range maintains a highly active mission training schedule and supports

multiple branches of DoD. Eglin AFB was very accommodating and provided in-kind services for access to the range, EOD support in characterizing the soils, setting up for the burn, conducting the burn, and post-burn sampling activities.

Approximately four acres of land located on Range C52 North (C52-N) in an area called the “Cat’s Eye” was selected as the location for the FERM Investigation. C52-N is predominantly an air-to-ground combat training area and was chosen because of its high rate of mission activity, known levels of energetic residuals in the surface soils, diverse vegetative cover, and the potential to monitor surface water runoff.

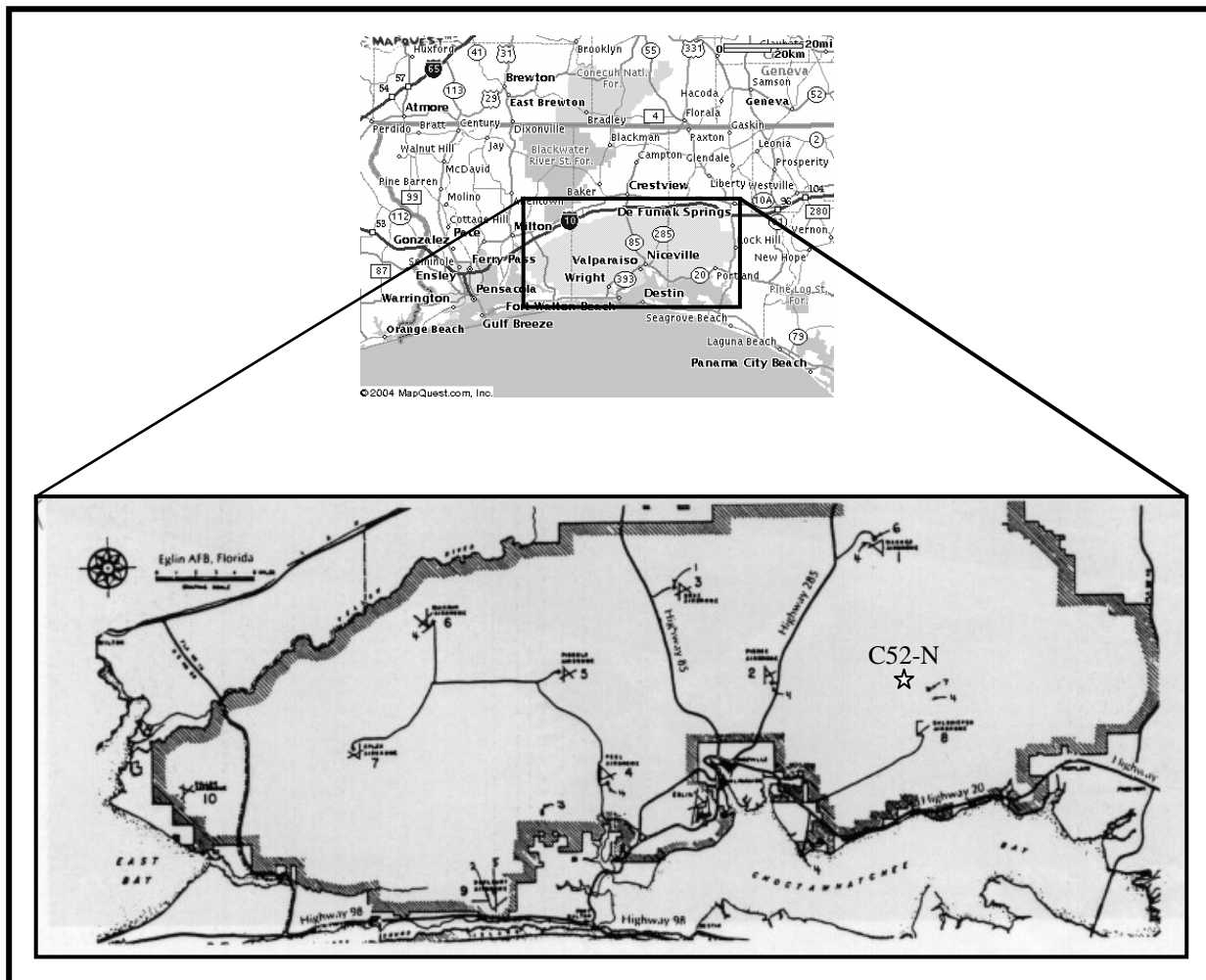


Figure 3-1. Site Map showing Eglin AFB and Range C-52-N

3.2 Laboratory Thermal Decomposition and Migration Testing

The primary objective of laboratory testing was to investigate the thermal decomposition of energetic residuals associated with soil at temperatures believed to be characteristic of a prescribed burn. Bench-scale experiments were conducted using soils collected from Sandia National Laboratory in Albuquerque, NM (referred to herein as Sandia soil), and from an uncontaminated location near the selected test

location at Eglin AFB, FL (referred to herein as Eglin soil). The soils were spiked with a known concentration of contaminant to determine the rates of decomposition and behavior of energetic materials at varied temperatures and soil moisture content. The TNT used in this study was manufactured in China and the RDX was extracted with acetone from C4. Approximately 8 grams of RDX was recovered from 12 grams of C4 after extraction and re-crystallization from acetone. The crystallized RDX product was ground into fine powder with a mortar/pestle.

The Eglin soil was dried for 240 hours at room temperature, passed through a 20-mesh sieve, and then sealed in a polyethylene bag and stored at room temperature. In the cases of the 0.1% (1,000 mg/kg) and 10% (100,000 mg/kg) TNT, the soil was homogeneously contaminated with TNT by adding a TNT acetone solution to the soil and tumbling the soil in a 500-mL round-bottom flask for 1 hour at 0°C (see Table 1). The soil was then spread out on a sheet of clean aluminum foil for one hour to evaporate the acetone and then returned to the round-bottom flask and rotary tumbled again overnight at 0°C. For the soil contaminated with 10 mg/kg TNT, 1 g of the 1,000 mg/kg TNT/soil mixture was tumbled overnight with 10 grams of uncontaminated Eglin soil; then another 90 grams of uncontaminated soil was added to the flask and tumbled overnight. A mixture of 10% RDX in soil was obtained by adding 5 grams of the powdered RDX to 45 grams of uncontaminated soil and tumbling, at a moderate rate (30 rpm) in a 250-mL flat bottom flask, for 3 hours. A 1,000-fold dilution (0.1%) of RDX in soil was obtained by diluting the 10% RDX contaminated soil with an appropriate amount of uncontaminated soil. To assess the homogeneity of the explosive in soil, five replicate soil samples (~0.1 g) were analyzed as described below. Variations in the amounts of explosive in the soils were within $\pm 5\%$. The unused TNT soil mixtures were stored at 20°C until needed. Unused RDX contaminated soil was stored at room temperature in a desiccator until needed.

The explosive-contaminated soil (0.5g) was placed in 2-mL sample vials (Agilent™, 11.4 mm outside diameter (o.d.) \times 32 mm), which were left open to the atmosphere. In some cases, immediately prior to heating, 5% water was added. Sealed samples were generally used for the neat explosives; these were flame sealed in pre-scored Wheaton ampoules of approximately the same dimensions as the sample vials (11.6-mm o.d.). The vials were heated in an oven for designated times; decomposition was quenched by removal from the oven and addition of acetonitrile. Samples heated to 100°C were stored at 15°C; those heated to 175°C or above were allowed to stand at room temperature. Once a complete set of samples was available for a given temperature, that batch of samples was analyzed as follows. Portions from each vial (~0.1 g) were accurately weighed into a 16-mL amber vial, extracted with acetonitrile (Table 3-1), sonicated for 30 minutes, and allowed to equilibrate overnight at room temperature. Residual soil was removed from the acetonitrile extract by filtration through a 0.2- μ m syringe filter (13-mm Millex-FG).

Quantification of the explosive solutions was accomplished using a liquid chromatograph (Agilent Model 1100 LC) equipped with a Agilent Hypersil BDS column and photodiode array detector (LC/PDA). A modification of a procedure developed by Agilent for analysis of TNT in soils was used (Agilent Pub. #5091-7626E). An isocratic solvent system consisting of 60 % (TNT) or 40% (RDX) methanol in water was employed and detector signals were monitored at two wavelengths, 214nm and 235nm. The sample injection volume was dependent on the explosive concentration (see Table 3-1). TNT and RDX peak areas were compared against standards of known concentration. At least four standard TNT or RDX solutions were prepared and analyzed in order to construct a standard curve. In addition, quality assurance (QA) samples were prepared and run after every third sample to ensure the quality of the chromatographic data. The LC procedure produced a linear dynamic range for TNT concentrations between approximately 2-ng/uL to 500-ng/ μ L with a 5- μ L injection, and 5-ng/uL to 2,500-ng/ μ L with a 1- μ L injection. To verify analyte recoveries, a spiked blank was prepared in acetonitrile using TNT or RDX. The ratio of the LC/PDA peak areas of a comparably spiked soil extract and the spiked blank gave the fraction of TNT or RDX recovered from the soil. Five replicates of this experiment were performed.

Recoveries of $95\% \pm 5\%$ were achieved. For soils with extremely low concentrations of TNT quantification was performed using an Agilent 6890N network gas chromatograph equipped with micro ECD and a HP-5 capillary column. Inlet temperature was held at 175°C , while the detector temperature was set at 250°C . Initial oven temperature was held at 50°C for 1 minute and increased at a rate of $20^{\circ}\text{C}/\text{min}$ until 200°C was reached. Holding time at the final temperature was 5 minutes.

Table 3-1. Extraction-Solvent and Injection Volumes for TNT and RDX Analysis

	TNT_{final soil}		Soil (g)	TNT (mg/kg)	Diluent	Acetonitrile (mL)	Injection Volume (μL)
	mg/kg	%					
TNT	10	0.001	100	1,000	Soil/soil	2	1 (GC)
	100	0.01	200	200	10 mL acetone	1	5 (LC)
	100,000	10	200	20,000	200 mL acetone	4	1 (LC)
RDX	100	0.01	200	1	Soil/soil	1	5
	100,000	10	45	5	Soil/soil	5	1

3.2.1 Explosives Decomposition Study. To investigate the production of decomposition gases, 10- to 15-mg of explosive-contaminated soil (0.1% and 10%) was heated to 250°C in sealed glass melting-point capillary tubes (5-cm length by 1.5- to 1.8-mm o.d.) for sufficient time to allow full and/or partial (TNT only) decomposition. Five replicates were prepared for each experimental condition. After heating, the tubes were returned to room temperature before being analyzed for N_2 , N_2O , CO , and CO_2 .

The samples were analyzed using gas chromatography. Capillary tubes containing the thermolyzed samples were placed in the sample loop made of 28-cm long flexible Nalgene™ tubing (0.32-cm inside diameter [i.d.] × 0.48-cm o.d.) and located in line with the carrier gas and just before the injector. After the sample loop was thoroughly purged with the helium, the gaseous decomposition products were released from the sealed capillary tube by sequentially crushing them by flexing the Nalgene™ tubing in which they were encased.

A Hewlett Packard 5890 gas chromatograph equipped with a thermal conductivity detector (TCD) and a packed column (Hayesep DB 100/120 mesh, 30-ft long × 0.125-in i.d.) was used to quantify the decomposition gases listed above. Resulting peaks were identified using both authentic samples and a gas chromatograph with a mass selective detector (GC/MS Hewlett Packard 5890/Hewlett Packard Model 5971 MSD with Chrompack Poraplot Q capillary column (25-m length × 0.25-mm i.d.). A standard-gas mixture (Scott Specialty Gases, 40% N_2 , 5% CO , 25% N_2O and 30% CO_2) along with fixed volume sample loops were used for instrument calibration. The GC inlet temperature was 120°C and the detector temperature was 200°C . The initial oven temperature was held at 50°C for 6 minutes, then ramped at $40^{\circ}\text{C}/\text{min}$ to 180°C and held for 20 minutes.

3.2.2 Explosives Migration Study. Glass soil columns were used to investigate thermal decomposition versus heat induced migration of TNT and RDX. Clean glass tube (55-cm length × 7.0-mm i.d.) were sealed on the bottom with cellophane tape and filled with uncontaminated soil. The tube was repeatedly tapped to achieve a moderately packed soil column that was approximately 5 cm in height. The position of the top of the clean soil was marked on the side of the column and approximately 3 g of TNT-contaminated soil (10%) was placed on the top of the clean soil. The tube was again tapped until the height of the contaminated soil was similar to that of the clean soil. The mass of contaminated soil added to each column was recorded.

In most studies, Thermolyne® heat tape (17-mm wide × 115-cm long) was wrapped around the outside of the column over the section that contained the TNT-contaminated soil (~ 5 cm) to induce a thermal gradient throughout the contaminated soil. A Thermolyne® type 45500 input controller was adjusted so that the middle of the contaminated soil column reached the set temperature (250°C for TNT; 250°C, 210°C, 200°C, or 180°C for RDX). The temperature in the soil was measured using an OMEGA on/off proportional controller (CN3920A) with a cable-mounted stainless steel probe. Following the heat cycle, the soil contents of the column was removed in 1-cm sections from the bottom of the tube, transferred into 16-mL amber vials, and then weighed for subsequent extraction for analysis. Acetonitrile (see Table 3-1 for volumes) was added to the each vial and the vials were then sealed. The contents of the vials were extracted in a sonicating water bath for 30 minutes, and then equilibrated overnight.

The empty tubing above the position of the top of the contaminated soil layer was cut into three discrete 9-cm sections. The inner wall of each section was rinsed with acetonitrile and TNT or RDX in the rinsate were quantified by the LC method described above. The total amount of explosive decomposed was calculated as the initial mass present in the contaminated soil layer minus the total sum of the explosive that migrated to clean soil, sublimed to wall of the empty tube, and remained in the originally contaminated soil.

To consider the possibility of formation of intermediate organic products during the process of RDX decomposition, samples from selected migration tests were analyzed by GC/MS (Agilent 6890A GC coupled to 5973 Inert Mass Selective Detector). The separation column was a HP5-MS (Agilent 19091J-433, 30-m length × 0.25-mm i.d., 0.25-um film thickness). The operating conditions were as follows: injector port temperature 170°C; 1-μL injection volume in splitless mode; helium carrier gas at flow 5.0 mL/min.; oven temperature program 50°C for 1.0 minute, ramp at 5°C/min to 160°C, then 10°C/min to 220°C and hold for 10 minutes. The mass spectrometer settings were as follows; electron impact ionization mode; ionizing energy 70 eV; scan range m/z 15 to 550 at 1.42 scan/sec.; ion source temperature 230°C; MS quad temperature 150°C; electron multiplier voltage maintained at 1480 V; solvent delay 4 min.

3.3 Initial Site Characterization

The initial site characterization occurred in April 2003 and included sampling soil and plant materials to obtain baseline data for the levels and distribution of explosive residues in the surface soil and in indigenous vegetation tissues; and making an assessment of the density and distribution of vegetation around the contaminated areas. These activities were important to locate the best placement for the test equipment, and to determine the propensity of native plant species to absorb/uptake energetic compounds from the soil since those compounds that are stored in aboveground portions of the plant are susceptible to destruction during burning. These issues were investigated through an assessment of energetic residual concentrations in surface soils from several locations around the investigation test area, an evaluation of the vegetation distribution, and analyses of native plant species tissues for energetic residuals as described below.

The area characterized was approximately 4 acres (Figure 3-2) located approximately 216 m from the north to south boundary and approximately 144 m from the east to west boundary of Range C52-N. The northernmost edge of the area sat at the crest of a hill that sloped to the south at a grade of approximately 7 m at the southernmost boundary of the area. The site had varied level of vegetation with a general increase in density toward the southern end. Surface soil and plant samples were collected from six key areas within the study area.

The first two areas characterized were air-to-ground target impact areas and were designated as Site 1 and Site 2. Site 1 was located on the south sloping side of the “Cat’s Eye”, and was the northern most of the

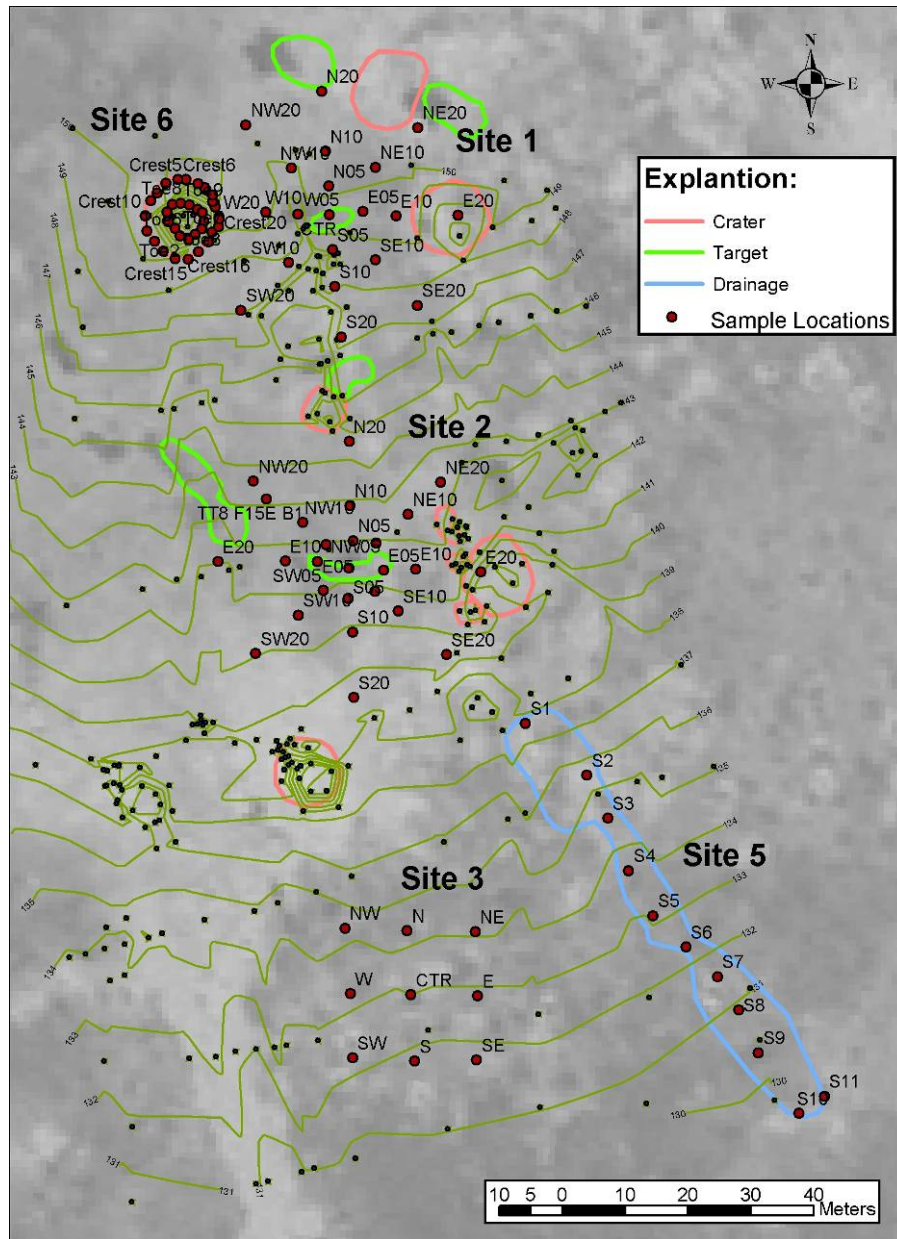


Figure 3-2. Study Area at Cat's Eye, C52-N, Eglin AFB

two characterized target areas. Site 2 was located approximately 15 m to the south of Site 1. Each site was sampled using a previously developed concentric-circle grid system similar to that shown in Figure 3-3. The grids each consisted of three concentric circles labeled Circle A, B, and C that were centered on the target impact point and had radii of 5m, 10m, and 20 m, respectively. Each circle was segmented as shown in Figure 3-3 and the four corners of each segment were logged using a differential global positioning system (dGPS).

Surface soils from these two sites were collected from each grid segment using stainless steel hand shovels with a stop-point built in so that only the top 3-4 cm of soil was sampled. Within each segment, 35 to 40 individual randomized surface soil samples were composited into one, 1-L wide-mouth amber

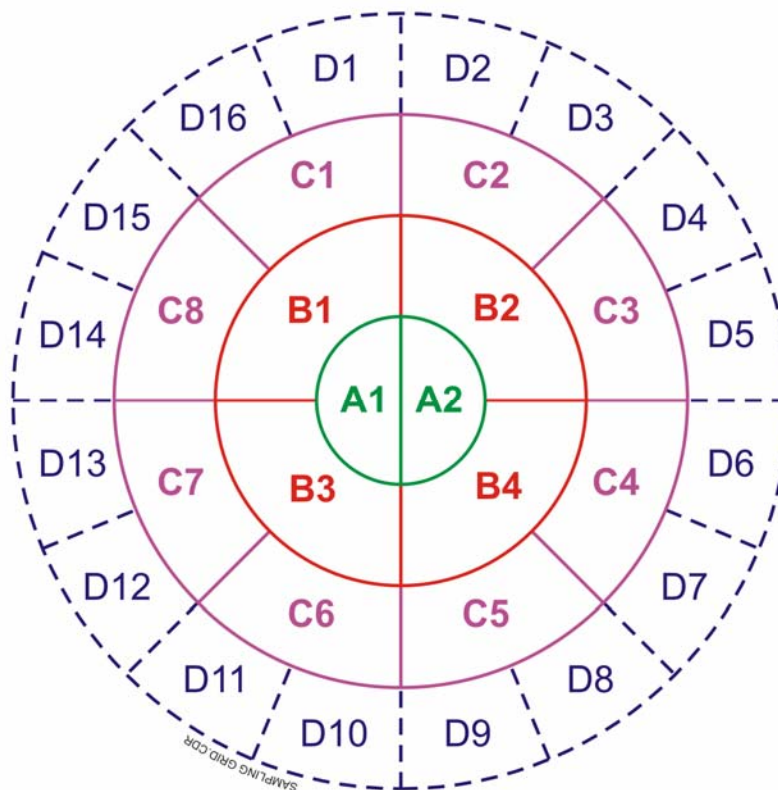


Figure 3-3. Conceptual Circular Grid and Segment Layout for Surface Soil and Vegetation Sampling at Site 1 and Site 2

glass jar with a TeflonTM-lined lid. The soils were stored in a cooler with ice until shipment later that day. Soil sampling equipment was decontaminated with acetone between sampling each segment.

Plant samples were randomly collected from within the grid segments at both sites. Photographs were taken prior to sampling to record the spatial distribution of plants within the grid area and the condition of indigenous plants prior to sampling. The aboveground tissue was removed by cutting with pruning scissors and the sample was transferred into a paper WhirlpackTM sample bag. The tissue samples were placed inside a cooler with ice and then transferred into a freezer until shipment to the laboratory for analysis of explosive residues.

Site 3 was located approximately 100 m south of Site 2 on a plateau at the base of the slope and had more vegetation than Sites 1 and 2. It was believed that this might be a collection point for surface residuals entrained in runoff from the northern section of the “Cat’s Eye”. A 20 m × 20 m square grid was setup within a section of the plateau area and partitioned into four 10 m × 10 m quadrants. The coordinates of four corners of the grid quadrants were recorded using dGPS. One composite soil sample was collected from each of the quadrant areas by combining 35-40 individual randomly collected surface samples, as described for Sites 1 and 2. Photographs of the vegetation were taken prior to sampling as described previously. Three aboveground plant tissue samples were collected from each quadrant for a total of 12 plant samples from Site 3.

Site 4 was located adjacent to the C52-N Control Station and was selected to serve as a background site based on the appearance that the area was not impacted from the training exercises. Two composited soil

samples were collected from this site following the compositing procedure used for the other sites. No plant samples were collected from the control area.

Site 5 was selected based on the visual evidence of significant surface water runoff. This "washout" area was located at the southern most edge of the study area boundary. Twelve surface soils samples were collected along a line transecting the washout bed and trending in a north-westerly to south-easterly direction. The soil was sampled using the randomized compositing approach described previously. Each sampling location was recorded using dGPS. No plant samples were collected from this area.

Site 6 was located adjacent to Site 1 and was a "blowhole" created from on-site detonation/disposal activities. Surface-soil samples were collected around the perimeter and inside the blowhole. No plants were present in or near the blowhole so no samples were collected.

Three surface water samples were collected from a creek that ran approximately 150 m south of Site 3. The samples were collected by hand-dipping a 1-L wide-mouth amber glass jar. The jar was completely filled and then sealed with a Teflon™-lined lid. The water samples were stored in a cooler with ice until being shipped via overnight delivery to the laboratory for analysis.

3.3.1 Sample Processing and Analytical Methods. Compositing-soil samples were shipped via overnight delivery to the Army's Cold Regions Research Engineering Laboratory (CRREL) for processing and analysis of explosive residues. The soil was passed through a #10 mesh sieve (2 mm) to remove small stones and pieces of metal. The sieved soil was machine ground on a LabTechonics™ ring mill (Labtech Essa Pty. Ltd., Bassendean, WA, Australia) for 70 seconds. The ground material was spread out in a pie pan and a 5.00 ± 0.02 -g compositing sample was prepared from approximately 15 portions of soil randomly collected from across the pie pan. The compositing samples were extracted and analyzed for explosive compounds using high-performance liquid chromatography (HPLC) following EPA SW-846 Method 8330 (EPA, 1997). Laboratory duplicates were prepared for approximately 20% of the compositing samples. The soil sample processing methods used were based on previously described methods (Walsh et. al, 2002).

Plant tissue samples were taken to the Eglin AFB, Natural Resources Branch at Jackson Guard where they were identified by a staff botanist. Table 3-2 shows the scientific and/or general nomenclature for each specimen collected during the characterization effort. After identification the samples were shipped via overnight delivery to Battelle's Laboratories in Columbus, OH for processing and explosives analysis.

The plant samples were weighed (± 0.5 g) and the weights were recorded. The samples were lightly rinsed with acetonitrile to remove and capture any residues on the tissue surface. The rinsate was collected in clean amber 1-L wide-mouth jars, which were sealed with Teflon™-lined lids. The samples were stored until extraction and analysis.

The plant tissues were processed and analyzed using the following method described by Larson (Larson et al., 1998). Plant tissue was cut into small pieces using a knife and placed into a homogenization pre-chamber. A volume of ultra-high purity water (Milli-Q™) was added to just cover the top of the sample. The contents of the chamber were homogenized on a laboratory mill at an initial speed of 500 revolutions per minute (rpm). The speed was incrementally increased to 2,500, 5,000, and 7,500 rpm. If the sample did not form a "frothy" slurry at this point, homogenization was continued at 10,000 rpm. The slurry sample was poured into a 120-ml freeze-drier flask, covered with Parafilm™, and then placed in a freezer until frozen (approximately 3 to 4 hours). The samples were then freeze-dried and transferred into 20-mL amber glass vials.

Table 3-2. Plant Tissue Sample Identification for C52-N Characterization

Location ^(a)	Segment/Quadrant ID	Plant Name
Site 1	A1	<i>Andropogon virginicus</i> (Broom Sedge)
	A1	<i>Andropogon virginicus</i> (Broom Sedge)
	B2	<i>Eupatorium compositifolium</i> (dog fennel)
	B2	<i>Yucca flaccida</i>
	B2	"Lawn Grass"
	C1	<i>Battisia lanceolata</i>
	C2	<i>Andropogon virginicus</i> (Broom Sedge)
	C2	<i>Andropogon virginicus</i> (Broom Sedge)
	C6	<i>Gaylussacia/Saccia</i> (Huckleberry)
	C8	<i>Andropogon virginicus</i> (Broom Sedge)
Site 2	A1	<i>Eupatorium compositifolium</i> (dog fennel)
	A2	<i>Eupatorium compositifolium</i> (dog fennel)
	A2	<i>Eupatorium compositifolium</i> (dog fennel)
	B2	<i>Eupatorium compositifolium</i> (dog fennel)
	B3	<i>Eupatorium compositifolium</i> (dog fennel)
	C3	<i>Yucca flaccida</i>
	C4	<i>Andropogon virginicus</i> (Broom Sedge)
	C6	<i>Andropogon virginicus</i> (Broom Sedge)
Site 3	Q1	<i>Andropogon virginicus</i> (Broom Sedge)
	Q1	<i>Quercus geminta</i> (Sand Live Oak)
	Q1	<i>Andropogon virginicus</i> (Broom Sedge)
	Q2	<i>Andropogon virginicus</i> (Broom Sedge)
	Q2	<i>Andropogon virginicus</i> (Broom Sedge)
	Q2	<i>Andropogon virginicus</i> (Broom Sedge)
	Q3	<i>Andropogon virginicus</i> (Broom Sedge)
	Q3	<i>Andropogon virginicus</i> (Broom Sedge)
	Q3	<i>Andropogon virginicus</i> (Broom Sedge)
	Q4	<i>Diosperus virginiana</i> (Persimon)
	Q4	<i>Andropogon virginicus</i> (Broom Sedge)
	Q4	<i>Andropogon virginicus</i> (Broom Sedge)

(a) Plant samples were not collected at Sites 4, 5 or 6

A, B, C = Circle A, B, or C (see Figure 3-3)

ID = Identification

Q = Quadrant (Site 3 only)

The samples and associated quality control samples were extracted with acetonitrile by swirling for 1 minute, then sonicating for 18 hours in a cooled ultrasonic water bath. After sonication, the samples were centrifuged at 2,500 rpm for 5 minutes and allowed to sit for approximately 1 hour before the extract was recovered. The supernatant was removed, processed through cleanup steps, and then analyzed using EPA SW 846 Method 8330.

3.3.2 Quality Assurance and Quality Control. Quality assurance/quality control (QA/QC) procedures were implemented in the field and in the laboratory to ensure production of meaningful test results. During field sampling activities, field duplicate (FD) samples were collected at a frequency of 20%. Precautions were taken to decontaminate equipment including the stainless steel shovels used for

surface-soil-sampling and the pruning shears used for plant sampling. Field equipment was decontaminated between sampling grid segments by rinsing thoroughly with acetone. Laboratory sieves used for soil processing were cleaned between sample composites in a similar manner. Glass sample bottles sealed with Teflon™-lined lids were used in an effort to reduce the sorption of contaminants. Whirlpack™ paper sample bags were used for plant samples, as plant tissue tends to break down more rapidly in plastic bags and glass bottles.

Chain-of-Custody (COC) procedures were adhered during shipment and handling of samples both in the field and in the laboratory. All samples were shipped via overnight delivery to the appropriate laboratory and were accompanied with a completed COC form that included the sample identification, sample date and time, number of samples, location of sample, name of the sampler(s), and the method of analysis. COC forms were signed and dated prior to shipment, placed inside a Ziplock™ bag, and taped to the inside lid of the coolers prior to shipment. Upon arrival at the laboratory, laboratory staff ensured that all sample containers arrived intact and then signed, dated, and recorded the sample receipt time. The COC followed the samples through the laboratory processing and analysis steps, and was signed appropriately as sample custodies changed.

Laboratory precision and accuracy for soil and plant tissue sample analyses were determined using the analytical results from laboratory duplicates (LD), analytical duplicates (AD), and blank matrix spikes (MS) that were analyzed at a frequency of 10%. Laboratory duplicates consisted of samples that were split after the grinding process. Analytical duplicates consisted of duplicate injections of the sample extract and were run to determine the analytical precision of the instrument for that given sample. Matrix spike samples consisted of clean soil from the site that had been spiked with a known mass of explosive compounds. Recovery of the spiked mass gave an indication of the extraction efficiency. Data quality was calculated as described below.

3.3.2.1 Precision. Precision for FD, LD and AD was calculated as the relative percent difference (RPD), whereas precision for three or more replicates was calculated as the relative standard deviation (RSD). These indicators of precision were calculated with the following two equations:

$$RPD = \frac{(C_1 - C_2) * 100\%}{(C_1 + C_2)/2} \quad (3-1)$$

where C1 = larger of two observed values
C2 = smaller of two observed values;

and

$$RSD = \frac{S}{\mu} * 100\% \quad (3-2)$$

where S = standard deviation
μ = mean of replicate analyses.

3.3.2.2 Accuracy. The accuracy of matrix spikes was determined using the following equation for recovery:

$$\text{Recovery}(\%) = \frac{(\text{Amount in spiked sample}) - (\text{Amount in background sample})}{(\text{Spike added})} \times 100\% \quad (3-3)$$

3.4 Field-Scale Prescribed Burn

The primary goal of the field-scale burn was to quantify the localized impact burning had on energetic residual concentrations in surface-soils. Secondary goals included measuring heat penetration into the soil column during burning and assessing post-burning infiltration and surface runoff. The prescribed burn was conducted on the active practice and training range. The following sections describe the test site layout and discuss the setup and preparation of the test site, pre- and post-burn sampling activities, and the burn procedure.

3.4.1 Pre-Burn Site Activities. The controlled burn was conducted in early August, 2004. The FERM Project Team (Team) mobilized to the site to setup the test systems and prepare for the pre-burn and post-burn sampling. Eglin AFB provided two on-site EOD specialists who monitored all of the work conducted on the range by the project team to ensure personnel safety. Three Rivers R&D, Inc., (Three Rivers) was contracted to provide labor support to distribute pine-straw on the burn area. Three Rivers was one of the few contract firms identified by Eglin AFB Range Safety that was suitable for performing this work. Pine straw was added to adjust the fuel load and to carry the fire more efficiently across the test area. All equipment needed to carry out the field execution was organized and loaded into a 24 foot box truck. The back of the truck provided a working platform for all preparatory work. The field execution consisted of the following pre-burn installation activities.

1. Prepared Test Soil with known explosives concentrations.
2. Established the boundaries of the burn area.
3. Identified and located four (4) test areas consisting of varied levels of fuel load, with one area to serve as the non-burn control area.
4. Laid out the coordinates of the grid system developed for each of the 4 test areas and recorded their coordinates using differential global positioning system (dGPS).
5. Conducted pre-burn surface-soil sampling in each of the 4 grid areas.
6. Installed thermocouple stations and data loggers systems in central locations for each of the four test areas.
7. Prepared and installed triplicate migration columns at each of the 4 test areas.
8. Prepared and installed triplicate TNT-melting columns at each of the 4 test areas.
9. Prepared and installed triplicate RDX-melting columns at each of the 4 test areas.
10. Prepared and installed Pyrex™ dishes and pans containing varying depths of soil previously characterized with known energetic concentrations and uncontaminated “control” soils at each of the 4 test areas.
11. Placed temperature monitoring strips at strategic locations across the burn area.
12. Distributed pine-straw over burn area in varying amounts to adjust the fuel load.

3.4.1.1 Test Soil Preparation. The Test Soil used for the various deployments was obtained from the U.S. Army Corps of Engineers Water Experimental Station-Engineering Research Development Center (USACE WES-ERDC), Vicksburg, MS. The Center acquired the weathered soil from a non-disclosed site at the Massachusetts Military Reservation (MMR) and provided Battelle with approximately 10 L of untreated, moderately characterized soil. Table 3-3 lists the physical/chemical properties of the test soil.

Table 3-3 Physical/Chemical Properties of the Test Soil from the Massachusetts Military Reservation.

Parameter	Value	Parameter	Value
% Sand	63.5	% Total Organic Carbon	0.6
% Silt	34.2	CEC (meq/100g)	5.6
% Clay	2.4	K (% saturation)	14.5
pH	6.74	Ca (% saturation)	50.4
% Organic Matter	0.8	Mg (% saturation)	30.7
		H (% saturation)	0

The soil was mixed in a cement mixer (~50 L capacity) for 24 hours with periodic water spray to control dust. After mixing, the soil was transferred to a 10-L bucket and then passed through a ¼-inch mesh sieve to remove larger rocks and debris. The sieved soil was placed back into the mixer and mixed for an additional 24 hours, and then transferred back into the 10-L container. Fifty 10-g grab samples were collected and composited in a glass sample jar, which was then emptied onto a 20 cm × 30 cm glass tray. The soil in the tray was sub-sampled by randomly removing 30 separate aliquots and compositing to a total approximate mass of 20 grams of soil that was extracted to determine the starting contaminant concentration of the Test Soil. This was repeated 9 additional times for a total of 10 composited samples for analyses. These data were averaged to determine the initial contaminant concentration of the soil. Energetic residual concentrations in the test soil were 2, 4, 6-TNT = $1,673 \pm 107$ mg/Kg; HMX = 11.8 ± 2.4 mg/Kg; RDX = 171 ± 62.0 mg/Kg; and 2A- 4,6-DNT = 4.4 ± 0.9 mg/Kg.

3.4.1.2 Test Site Layout. The burn block boundaries at the Cats Eye were Coon Head Branch to the east, Bay Head Branch to the west, and Range Road 200 to the north. The confluence of the two creeks to the south served as the southern boundary. The area bounded by these features covered approximately 150 acres. The test site was divided into 4 discrete test areas identified as E1 through E4. The positioning of those areas is shown as an overlay on an aerial site photograph Figure 3-4. Test areas E-1, E-2, and E-3 were located near locations that were sampled during the initial characterization (see Section 3.3) and shown to be contaminated sufficiently to allow tracking the fate of the explosives residuals before and after the burn. Exact positioning of the test areas on the coordinates from the initial characterization was not possible due to the placement of new targets and blowhole formations that had materialized over the elapsed time.

Test area E-1 was established in the north burn area and thus at the most elevated level of the site, as the site decreased in elevation to the south. Test area E-1 was the least vegetated area of the site and was supplied with a loading of approximately 3.7 tons/acre of pine straw. Test area E-2 was established approximately 20 m to the southwest of E-1. Area E-2 was characterized as having low to moderate vegetative density and was supplied with an additional approximate 7.0 tons/acre of pine straw. Test area E-3 was established at the south end of the burn site approximately 10 m away from a “blowhole” or impact area. E-3 was placed in an area of increased vegetative density and was positioned on level ground where the hill plateaus. A loading of approximately 12.5 tons/acre of pine straw was added to the E-3 area. Test area E-4 was designated as the non-burn control area. Area E-4 was approximately 40 m to the north of the northern most boundary of the burn area, yet close enough to the burn area to be subject to all other site exposures.

3.4.1.3 Test Area Layout and Test Systems. The four test areas were layed out according to a concentric-circle grid system that was similar to the grid used for the initial site characterization sampling and as shown in Figure 3-5. The radii for Circles A, B, and C were 5, 10, and 15 meters, respectively.

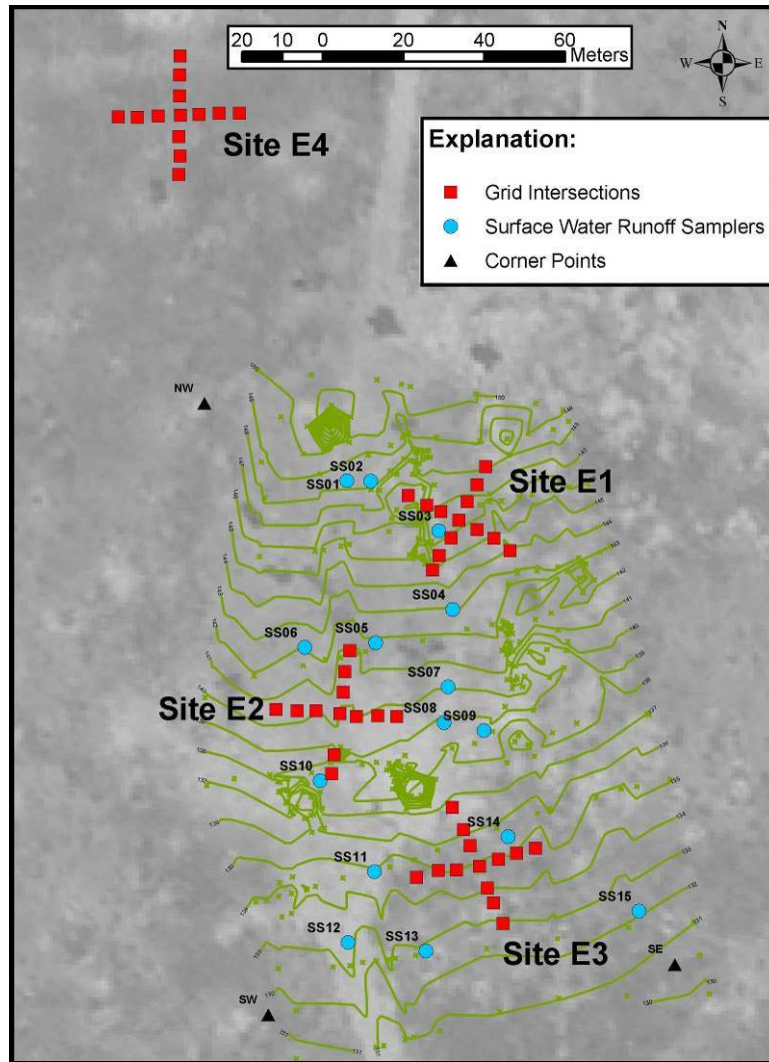


Figure 3-4 Burn Perimeter Containing Test Areas at Cat's Eye, C52-N, Eglin AFB

The area within Circle A was divided into two segments. The area between Circle A and Circle B was divided into 4 segments, and the area between Circle B and Circle C was divided into 8 segments. The coordinates for the four corners of each grid segment were logged using dGPS.

The grids were used to guide surface-soil collection and to locate various test systems and equipment including temperature recording thermocouple stations, temperature indicating strips, Pyrex™ dishes and pans containing Test Soil, migration columns, and explosives melting columns. Figure 3-5 shows the placement of the thermocouple stations, dishes and pans, and migration and melting columns. The following sections describe each system.

Thermocouple Stations and Temperature Indicators. Multi-level thermocouple stations and data loggers were located within Sphere A of each of the 4 test areas. Figure 3-6 is a schematic showing the thermocouple station setup. In an effort to not underestimate the potential for extreme temperatures, thermocouples with the capacity to withstand and accurately measure temperatures up to 1000°C were purchased and used for this effort (Vulcan Technologies, NJ). Each of the thermocouples were calibrated

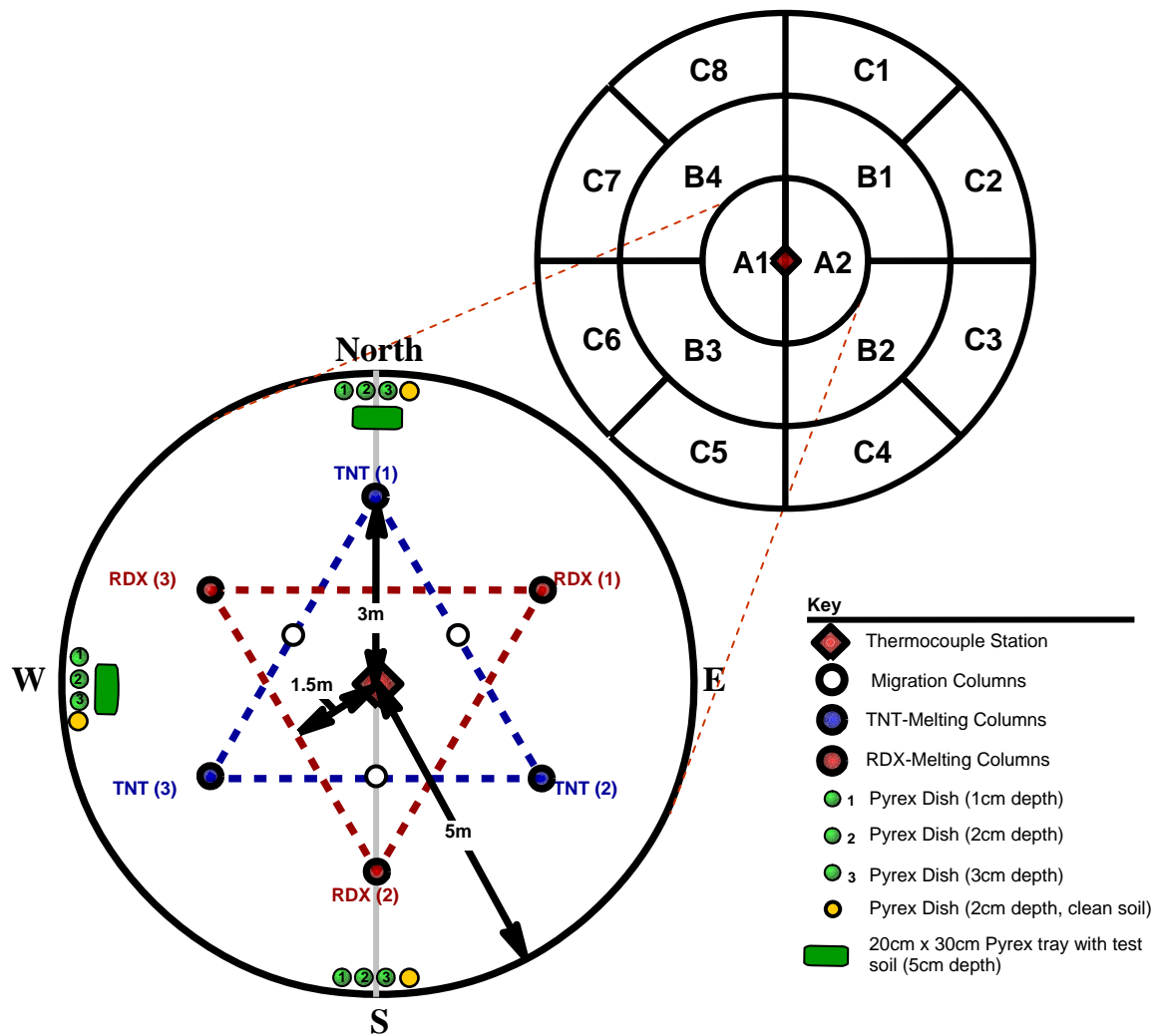


Figure 3-5. Circular Grid and Deployment Layout for Surface Soil Sampling and Test Soil Deployments at Study Areas E-1, E-2, E-3, and E-4

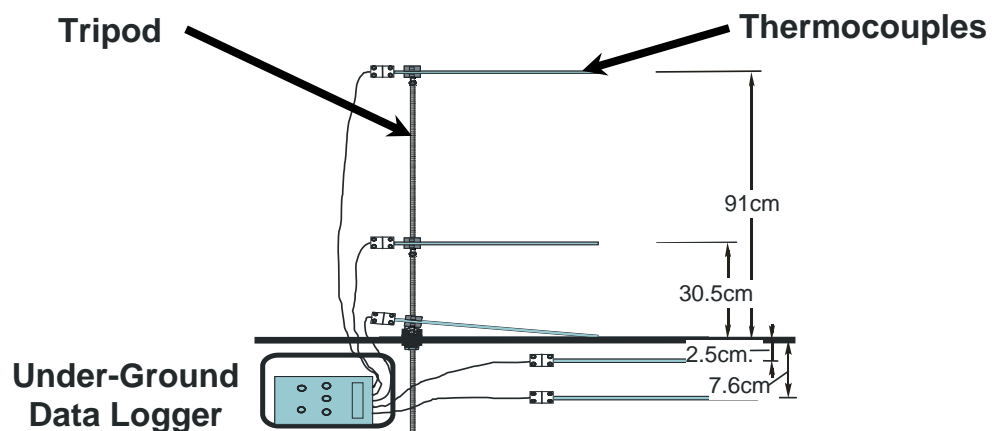


Figure 3-6. Thermocouple and Data Logger Station and Temperature Indicators

with a 10-point calibration of 100°C increments. The thermocouples were fixed to a metal tripod for stabilization. There were six thermocouples at each station. The first and second were positioned 91 and 30.5 cm above the ground surface (ags), respectively; two were positioned on the ground surface extending in the North and south directions approximately 1 m away from the tripod; and the last two were positioned below the ground surface (bgs) at 2.5 and 7.6 cm, respectively. The component end of each of two thermocouples was wired to a HOBO™ dual channel data logger (Forestry Supplier, Inc.) that were activated to receive temperature readings on 1 second intervals over the course of the burn period. The data loggers were enoused in a water-tight box that was sealed and buried below the ground surface and additionally insulated with fiberglass insulation under an inverted galvanized bucket. Figure 3-7 shows the thermocouple station and the data loggers inside the water-tight box.

In addition to the thermocouple station, temperature indicator strips were placed in various places around the test area for temperature estimations and to determine if the heat of the fire reached surface temperatures conducive to energetic destruction as tested in the laboratory at URI. These indicators were placed within the center of each of the grid segments, next to surface deployments of Test Soil and columns and within the bottom of each of the 7 cm dishes (Figure 3-7 shows the temperature strips as inside the dish deployments). When exposed to heat, the temperature indicators undergo a non-reversible color reaction within a specified temperature range, usually in 10°C to 25°C increments depending on the maximum detection level of the various indicators. The indicators used in this study had variable maximum detection levels ranging from 40°C to 270°C.



Figure 3-7. Photographs of the Thermocouple Station, Data Logger, and Temperature Indicator Strips

Test Soil Dishes and Trays. Pyrex™ glass dishes and trays were selected to contain Test Soil during the burn in an effort to minimize heat transfer associated with the container material. Pyrex™ dishes (7-cm diameter) were set up in triplicate with the volume of Test Soil required to achieve soil thicknesses of 1, 2, or 3 cm. An additional set of dishes was set up with 2 cm of clean uncontaminated soil to serve as the control to measure potential deposition of explosives compounds in settled ash. Each dish contained a temperature indicator strip that was placed on the inside bottom of the dish to measure the maximum temperature reached at the depth of the soil as the fire passed over the soil surface. The amount of Test Soil in each dish and the soil thickness and soil weight was recorded. Pyrex™ trays (20 cm x 30 cm) with 5 cm of Test Soil were set up in duplicate.

The dishes and trays were placed on the north, west, and south sides of Circle A, approximately 5 m from the centralized thermocouple station. Each side of the test area received 4 dishes, one of each Test Soil thickness and one Control dish. The dishes were set into the ground so that the top of the Test Soil was even with the ground surface. The trays were placed on the ground surface.

Residual Explosives Migration Columns. Columns were used to examine the potential for heat induced migration of explosives in soil. Pyrex tubing (30-cm long x 2.5-cm i.d.) was capped on the bottom end with a compression fitting and filled with clean play sand purchased from Lowes Home and Garden Center, Columbus, OH. The sand was packed repeatedly with a wooden rod and filled to the upper 5 cm of the tube. A 1.25-cm layer of Test Soil was placed on top of the clean soil, covered with a Teflon™ sheet, and then a rubber stopper was pushed into the column and up against the Teflon™ sheet to secure the soil layers for transport.

Three columns were placed along the Circle A grid line of each test area by boring a 5-cm diameter hole to a depth of approximately 25 cm with a hand driven bucket auger. The columns were placed into the borehole, which then was backfilled with native soil so that the top of the Test Soil inside the column was even with the soil outside the column and the unfilled portion of the tube extended approximately 5 cm above the ground surface.

TNT and RDX Melting Columns. Columns also were used to evaluate fate, destruction or melting, of neat TNT and RDX during burning. The columns were constructed from the same Pyrex tubing used for the migration columns described above. The columns were 15 cm long and triplicate columns were set up with uncontaminated sand to examine TNT and RDX separately. The columns were set up along the Circle A perimeter in each test plot by coring to approximately 15 cm below grade, placing the column in the hole, and completing the hole as described above. Just prior to initiating the burn, approximately 1g of neat TNT or RDX was placed onto the surface of the uncontaminated layer within the column.

3.4.1.4 Pre-burn Surface-Soil Sampling. Soil samples were collected from the top 2 to 3 centimeters of each of the grid segments using stainless steel hand trowels as described in Section 3.3. Forty (40) individual samples were collected from randomized locations and composited into one sample in a 1-L wide-mouth amber-glass jar. The jars were sealed with a Teflon™-lined lid and placed in a cooler with ice until they were transported off-site where they were stored in a refrigerator held at 4°C for one additional day. Soil-sampling equipment was decontaminated with acetone rinses between each segment.

3.4.1.5 Pine Straw Spreading. Pine straw was spread by hand across the test site to carry the fire with the amount placed in each of the four test areas adjusted to vary the fuel loads at an additional approximate 3.7, 7.0, and 12.5 tons of fuel per acre, for test plots E-1, E-2, and E-3, respectively (Note: native vegetation was not included in this estimate, however the native vegetation at test areas E-1 and E-2 was quite sparse, estimated by Eglin fire staff to be less than 0.5 tons per acre. At test area E-3, native



Figure 3-8. Migration Column Exposed to Fire

fuel was more abundant and estimated to be 1.5-2.0 tons per acre). A mechanical means of spreading the straw was not possible due to safety concerns regarding ordnance and vast amount of metal debris, which prohibited maneuvering a thrower and offered the threat of tire puncture. Pine straw was not added in or adjacent to the non-burn control area. Pine straw spreading required approximately 1.5 days to complete.

3.4.2 Controlled Burning. Jackson Guard planned the burn component of the field activities and designed a burn plan with the objective of consuming the Cat's Eye impact site at C52-N. The goal was to achieve a thorough burn with minimal residual smoke within the study site. The approach included placing auxiliary fuel, igniting the fire, and controlling the burn as it moved across the site. Fire management personnel from Jackson Guard were responsible for igniting the burn, controlling the spread of the fire, and determining when the fire was extinguished to allow access to perform post burn activities. The Fire Team managed the burn primarily by rapid ignition achieved via helicopter. No project team personnel were allowed on site during the burn or after the burn until final clearance was given from the Fire Boss and Eglin EOD.



Figure 3-9. Spreading Pine Straw at Test Area E-2

Eglin AFB's Fire Ecology Branch at Jackson Guard ignited the fire from a helicopter using a Primo Mark V Plastic Sphere dispenser, which ejected ethylene glycol ping pong ball-sized spheres filled with potassium permanganate. Aerial ignition was planned to minimize the risks associated with UXO. The fire was lit by making several passes along the northern boundary of the site. Fire Ecology staff monitored the fire and were on hand to take precautions to control and contain the fire within the test area.

Jackson Guard developed the approach immediately prior to the conducting the burn, taking into account several site factors including: (1) the risks of UXO associated with the site, (2) the need to minimize residual smoke and smoldering fire such that researchers can enter the area following the 24-hour cool-down period required by EOD guidelines, and (3) current weather conditions.

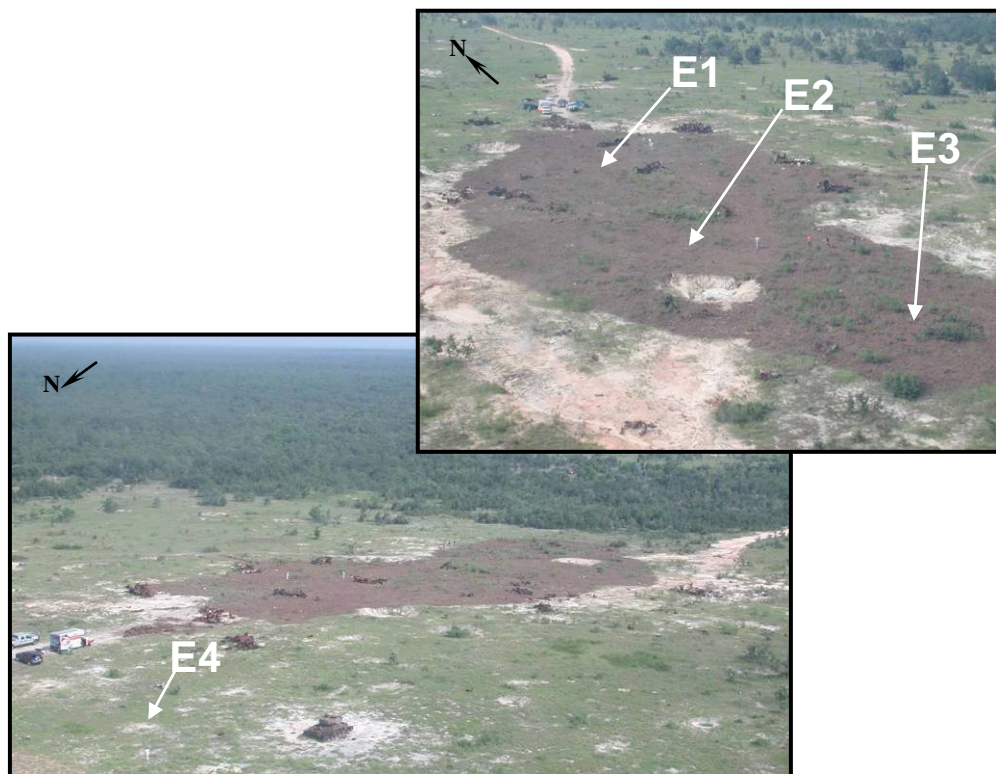


Figure 3-10. Prepared Test Site with Added Pine Straw Showing Locations of Test Areas

Due to safety concerns, the FERM project team was required to evacuate the site prior to ignition and remain off-site for a 24-hour cool down period after the fire was extinguished. The Team observed the burn from a distance of approximately 2 miles away on top of the C52-N control tower.

3.4.3 Post-Burn Site Activities. After the 24-hour cool-down period, the Team re-entered the site and conducted the following post-burn activities.

1. Conducted post-burn surface-soil sampling.
2. Retrieved the thermocouple stations, data loggers, and recorded the temperatures indicated on the test strips.
3. Retrieved the contaminant-migration columns.
4. Retrieved the TNT-melting and RDX-melting columns.



Figure 3-11. Fire Ignition at C52-N

5. Retrieved the dishes and trays containing the Test Soil.
6. Installation and sampling of surface water/sediment collection traps.

3.4.3.1 Post-Burn Sampling. Post-burn sampling included collecting surface soil samples across the test plots and collecting the Test Soil from the dishes and trays as follows (Figure 3-12).

Post-Burn Surface-Soil Sampling. The test areas and grid coordinates were re-identified and confirmed using dGPS. Grid nodes were re-marked with fresh flags and 35-40 surface soils grab samples were collected and combined into one sample, resulting in one composite sample per grid segment, as described previously. Post burn grid samples were stored on ice and were processed and shipped as described previously.



Figure 3-12. Post-Fire Sampling and Retrieval Activities

Post-Burn Test-Soil Retrieval. The soils in dishes and trays and associated uncontaminated controls were removed and transferred into 1L amber bottles with Teflon™-lined lids. Tray samples were transferred into 2L bottles. The temperature values on the indicator strips that were fixed to the bottom of the dish were recorded in the field record book and the sample jars were packaged on ice.

The samples and test equipment were transported to the box truck and the truck was driven to a location away from the test site where the samples were packaged with chain-of-custody forms and shipped via overnight express to Battelle's Labs in Columbus, OH, for processing and analysis.

3.4.3.2 Retrieval of Thermocouples and Data Loggers. Thermocouple stations were disassembled in the field and the data loggers were unburied and recovered. The data loggers were transported off-range and the data was downloaded to a computer and backed-up on a CD.

3.4.3.3 Migration Column Retrieval. The migration columns were retrieved by carefully sealing the exposed opening of the tube with a sheet of Teflon™ paper and a rubber stopper. The plug was secured and then the soil around the outside of the column was loosened and removed so that the column could be recovered by pulling it out of the ground. Each column was carefully packaged to prevent breakage and shipped on ice back to Battelle for bench-scale leaching tests and soil contaminant profiling.

3.4.3.4 Melting Column Retrieval. The TNT and RDX melting columns were retrieved in a similar manner. These columns were shipped back to the lab for extrusion, extraction and analysis.

3.4.3.5 Surface-Runoff Trap Installation and Sampling. The day after all the samples and test equipment were retrieved, 15 surface-runoff traps were installed at strategic locations where it appeared that runoff was channeled during storm events.

The traps were designed so that a retrievable and replaceable sample bottle was located below grade at the back end of the funnel section (Figure 3-13). The traps were installed so that the wider opening faced upstream and parallel to flow. The sample bottle was filled as runoff exited out the down-gradient side of the trap.

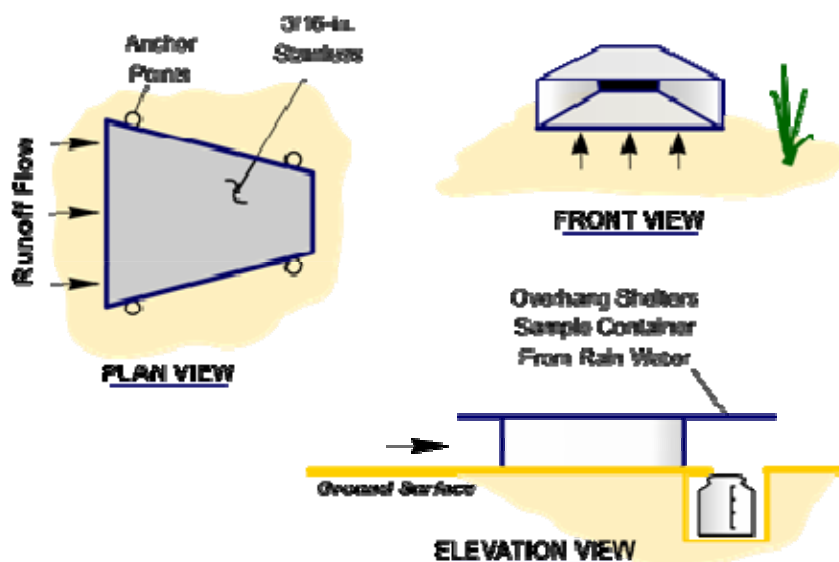


Figure 3-13. Surface Runoff Traps

The traps were installed pseudo-randomly in or nearby locations where there was visual evidence that surface water runoff flowed in the past (i.e., areas of gulley formation or washout plains). To place each unit, a small hole approximately 30 cm deep and 10 cm in diameter was dug in the soil. The collection end of the trap was placed in this hole and the front end (funnel end) was placed to receive the down flowing water sample, Figure 3-14.



Figure 3-14. Surface Water Trap Installation

The front end of the trap was secured into the soil with two 30 cm spikes. After it was secured an open bottle was loaded into the receiving end of the trap and a weather shield was secured to the unit. The weather shield was designed to prevent rain water from entering the opening of the jar before falling onto the ground surface.

The coordinates of each trap were recorded using dGPS. The installation of the surface traps comprised the last on-range activity. The traps were installed on Monday, August 9, 2004, and were first sampled on Friday August 13, 2004 after tropical storm Bonnie moved through the area and site access could be arranged.

The bottles were removed from the trap and the traps were recharged with new sample bottles. The water and sediment samples were shipped via overnight express to Battelle's Labs in Columbus, OH for processing and analysis of energetic residuals.

The second sampling was conducted on Monday August 23, 2004, after Hurricane Charlie moved through the area and site access could be obtained. The bottles were packed up and shipped to Battelle's Labs in Columbus, OH for processing and analysis as described previously. The traps were charged with new bottles and have not been sampled since. The traps were left in place for potential future sampling events

and it is not known whether or not the surface traps still remain or have been subject to destruction from mission activities on the range.

3.4.4 Post-Burn Laboratory Procedures. Surface soil and dish and pan soils, and the intact migration and melting columns were received by the labs, logged, and placed under refrigeration at $4\pm3^{\circ}\text{C}$ until processing. The migration columns were leached, and the migration columns were segmented as described below. The totality of the soils, sediments, water, and leachates were processed, extracted, and analyzed as described in the following sections using methods established by Walsh et. al. (2002).

3.4.4.1 Migration Column Processing. Leaching experiments were conducted on the migration columns once they arrived to the laboratory to determine the destruction of neat material and to determine if there was any downward migration of TNT or RDX as a result of the high temperatures achieved during the burn. The columns were positioned vertically with the contaminated Test Soil positioned at the top and the upper and lower caps were removed. A modified cap containing a fine mesh screen was fixed to the bottom of the column. A graduated burette was placed directly above, and a graduated cylinder was placed directly below, each column. Milli-Q™ (18 Mohm) water was added to the top of each column at approximately 5 mL per hour until 15 mL was collected in the graduated cylinder. The leachate was collected, passed through a 0.2- μm filter, and then stored in labeled vials under refrigeration until extraction for explosives analyses. The soil was extruded from the columns and partitioned into discrete depth intervals of 0-2.5 cm; 2.5-8.9 cm; 8.9- 15.2 cm; 15.2-21.6 cm; and 21.6- 28 cm, containerized, and stored under refrigeration until processing for analysis.

3.4.4.2 Melting Column Processing. The soil was extruded from the columns and the top 6.35 cm of soil was divided into depth intervals of 0-1.3 cm, 1.3 to 3.8 cm and 3.8 to 6.35 cm. The soil below 6.35cm depth was transferred to a 250 mL amber glass sample jar, sealed with a Teflon™-lined lid, and then archived.

3.4.4.3 Soil Processing. Surface soil, Test Soil, and soils from the columns were processed for sample extraction and analysis according to the following protocols.

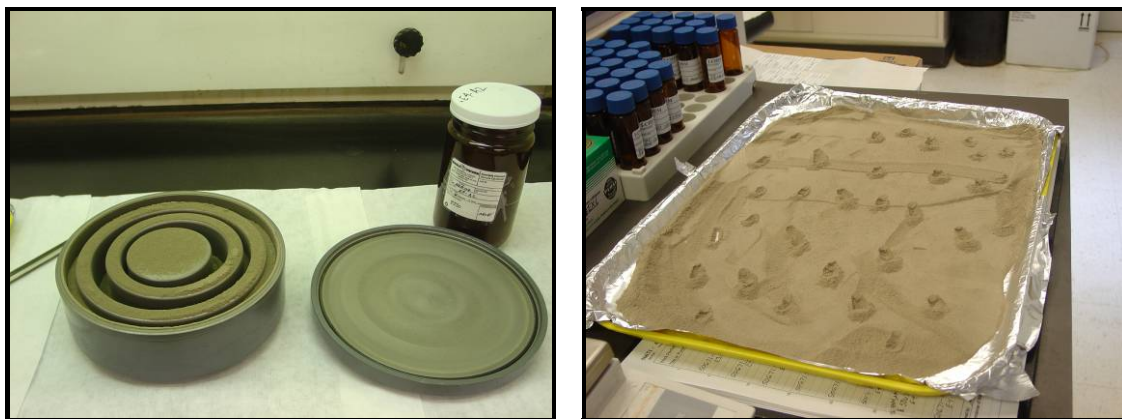


Figure 3-15. Soil Processing in the Laboratory Using Ring and Puck Mill Grinder and Compositing Plan

Surface soil, dish soil, and pan soil processing. Aluminum pans made from heavy-duty aluminum foil and large enough to allow the sample to be spread out to a uniform depth of approximately 3 mm were used to air dry each soil sample for between 24 and 48 hours under minimal lighting conditions (Figure 3-15). The dried samples were sieved using a No. 10 (2 mm) metal sieve, any remaining soil clumps were broken up in the sieve using a ceramic pestle. The material retained in the sieve was placed in a labeled Ziploc™ bag and stored under refrigeration. The weight of the sieved soil was measured and recorded.

The dry/sieved soil was ground in a puck mill grinder (Figure 3-15) for 1 to 1.5 minutes. The ground sample was thoroughly mixed and spread uniformly to a depth of 3 mm in a sub-sampling tray. The sub-sampling tray was a large plastic tray, which was wrapped with clean heavy-duty aluminum foil for each sample. The ground sample weight was obtained and recorded. A minimum of thirty grab samples were collected from across the sub-sampling tray to retrieve 10 grams of soil for extraction. The extraction samples were weighed and the weights recorded. The remaining soil was placed back into the original container and archived at 4±3°C.

Test soil that was generated from the dishes was subjected to drying and then the full soil volume was extracted. Therefore, the soil was not sieved, ground or sub-sampled because it had already been processed prior to being exposed in the field.

Migration and melting column soil processing. The dried and sieved soils from the migration and melting columns did not undergo any further processing (i.e., grinding) prior to extraction.

Sediment trap sample processing. Samples were separated into water and soil portions using a Buchner funnel and paper filter (Whatman #12). The filter paper was pre-wetted with HPLC-grade water. The whole sample was slowly transferred from the sample bottle to the funnel while vacuum was applied. The vacuum was left on until the soil in the funnel appeared dry and the water collection ceased. The volume of filtered water was measured and recorded and the water was transferred from the flask to labeled glass containers. The soil was spread out to a uniform depth of 3 mm in labeled aluminum pans and air dried for between 24 and 48 hours under minimal lighting conditions. The dried soils were sieved, grinded, and sub-sampled as described for the surface soil samples.

3.4.4.4 Sample Extraction. Soils, leachate, and runoff water samples were extracted using the following protocols.

Soil extraction. Acetonitrile (HPLC grade) at a volume in mL approximately double to the mass in grams was added to each sample. The samples were then extracted in an ultrasonic bath that was kept at room temperature or lower for eighteen hours. The samples were removed from the ultrasonic bath and allowed to settle for a minimum of one hour. Approximately 10 mL of each sample extract was removed and placed into a disposable syringe fitted with a 0.45-µm Pall Gelman™ PTFE filter. Approximately the first 2 mL of filtered extract was discarded as waste and the remaining 8 mL was transferred into a labeled amber two-dram vial. The remaining sample extract was archived at 1-7°C. The filtered extract was stored at 1-7°C until analysis. Prior to analysis, each sample was diluted 1:1 with 5 g/L calcium chloride.

Migration column leachate extraction. Five mL of each leachate was used for extraction. Acetonitrile (HPLC grade) at a volume in mL equal to that of the sample was added to each sample. The samples were then mixed by a vigorous hand shaking for ~ one minute. All remaining leachate was archived at 1-7°C. The 10-mL water/acetonitrile sample extract was removed and placed into a disposable syringe fitted with a 0.45-µm Pall Gelman™ PTFE filter. Approximately the first 2 mL of filtered extract was

discarded as waste and the remaining 8 mL was transferred into a labeled amber two-dram vial. The filtered extract was stored at 1-7°C until analysis.

Surface trap water extraction. Five mL of acetonitrile (HPLC grade) was added to 5 mL of each water sample. The contents were extracted by vigorously hand shaking for ~ one minute. The resulting 10 mL water/acetonitrile mixture was removed and placed into a disposable syringe fitted with a 0.45 µm Pall Gelman™ PTFE filter. The first 2 mL of filtered sample was discarded as waste and the remaining 8 mL was transferred into a labeled amber two-dram vial. The filtered extract was stored at 1-7°C until analysis. All remaining water was archived at 1-7°C.

3.4.4.5 Sample Analysis. The extracts were analyzed for explosives and the pH of the soil and leachate from the migration columns were measured as described below.

Explosives Analyses. Samples generated under FERM were analyzed for HMX, RDX, m-Dinitrobenzene (1,3-DNB), Methyl-2,4,6-trinitrophenylnitramine (Tetryl), Nitrobenzene (NB), TNT, 2-Amino-4,6-dinitrotoluene (2-Amino-4,6-DNT), 4-Amino-2,6-dinitrotoluene (4-Amino-4,6 DNT), 2,4-Dinitrotoluene (2,4-DNT), 2,6-Dinitrotoluene (2,6-DNT), o-Nitrotoluene (2-NT), m-Nitrotoluene (3-NT) and p-Nitrotoluene (4-NT). The analytical method used for explosives analysis was based on general procedures of SW-846 Method 8330. The analytical method consisted of a reversed-phase isocratic HPLC separation followed by UV detection for the fifteen analytes. The instrument parameters and specifics of the chromatography are presented in Table 3-4.

Table 3-4. Analytical Parameters for Explosives Analysis

HPLC/UV System	Dionex GP40	
HPLC UV Detector	Dionex AD20	
Software	PeakNet version 5.21	
Primary Analytical Column	Supelco LC-18, 5µm, 25 cm x 4.6mm, Catalog#: 58298	
Secondary Analytical Column	Supelco LC-CN, 5 µm, 25 cm x 4.6 mm, Catalog#: 58231	
Mobile Phase	50:50 Methanol (HPLC Grade): Water (HPLC Grade)	
Injection Volume	100 µL	
Flow Rate	1.50 mL/min	
Approx Retention Times using Primary Column	HMX: 2 min. RDX: 3 min. 1,3,5-TNB: 4 min. 1,2-DNB: 4 min. 1,3 DNB: 5 min. Tetryl: 5 min. NB: 6 min. 2,4,6-TNT: 6 min. 2-Amino-4,6-DNT: 7 min. 4-Amino-2,6-DNT: 7 min. 2,4-DNT: 8 min. 2,6-DNT: 8 min. 2-NT: 9 min. 4-NT: 10 min. 3-NT: 11 min.	
Approx Retention Times using Secondary Column	HMX: 11 min. RDX: 7 min. 1,3,5-TNB: 4 min. 1,2-DNB: 5 min. 1,3 DNB: 4 min. Tetryl: 8 min. NB: 3 min. 2,4,6-TNT: 5 min. 2-Amino-4,6-DNT: 6 min. 4-Amino-2,6-DNT: 5 min. 2,4-DNT: 5 min. 2,6-DNT: 5 min. 2-NT: 4 min. 4-NT: 4 min. 3-NT: 4 min.	
Run Time	20 min	

The HPLC was calibrated with a five-point calibration curve that covered a 100-fold range using standards at 0.25, 0.75, 3, 6, 25 µg/mL for each of the analytes listed above. Standards were stored at 1-7°C and were remade every 30 days or less as needed. Calibration curves were constructed in PeakNet plotting the UV area versus the standard concentration. Linear regressions were used to calculate a response factor that was applied to the peak areas generated during sample analysis to calculate the concentrations for each of the 15 analytes.

Analytical run sequences included at least one water blank followed by the calibration curve analyzed in order from low to high concentration. After at least one water blank, the FERM sample extracts were analyzed. Verification of analyte presence was accomplished by retention times on both the primary and secondary columns. The primary column results were used for quantitation. The secondary column results were used for confirmation.

Analytical quality control included reinjection of the 0.75-µg/mL calibration standard after no more than ten sample injections and at the end of the run to monitor instrument performance, these were called calibration check verification (CCV) standards. The CCV quantitated values had to agree within $\pm 15\%$ of the initial calibration in order for the sample values that were obtained between them to be accepted.

pH Analysis. Soil pH was measured in accordance with SW-846 Method 9045B. Aqueous sample pH was measured following SW-846 Method 9040.

3.4.5 Quality Assurance and Quality Control Quality assurance and quality control (QA/QC) was implemented in the field and in the laboratory to ensure the production of meaningful test results.

3.4.5.1 Field Quality Assurance. All surface soil samples were collected in the field in glass sample bottles and sealed with a Teflon™-lined lid to minimize sorption of contaminants onto container surfaces. Each bottle was labeled with the sample ID information, the initials of the sampler, the date and time of collection, and the required analyses. The bottles were wrapped in bubble wrap and placed inside a plastic liner inside a cooler. A chain-of-custody (COC) form was filled out with the sample identification, sample date and time, number of samples included in the cooler, location of sample collection, name of the sampler(s), and required method of analysis. The form was sealed inside a plastic bag and taped to the inside lid of each cooler. The cooler was loaded with wet ice, sealed with strapping tape, and then shipped via overnight delivery to Battelle's Laboratory in Columbus, OH.

One FD was collected from a randomly selected location in each grid segment prior to, and after, the burn. The stainless steel shovels that were used for collecting surface soil samples were decontaminated between each segment sampling with acetone and a distilled water rinse.

3.4.5.2 Laboratory Quality Assurance. In the laboratory all equipment that came into contact with the sample was decontaminated prior to using on additional samples to minimize the risk of cross contamination. This included the components of the puck and ring mill, spatulas, and drying trays, and solvent glassware.

Upon arrival, laboratory staff ensured that all sample containers arrived intact and signed, dated, and recorded the time that the samples were received in the laboratory onto the COC. The COC followed the samples through the laboratory processing and analysis steps, and was signed appropriately as sample custodies changed.

Laboratory precision and accuracy were performed through the analysis of LDs, ADs, and blank matrix spikes at a frequency of 5%. Laboratory duplicates consisted of samples that were split after the grinding process. Analytical duplicates consisted of duplicate injections of the same sample extract to determine

the analytical precision of the instrument for that given sample. Matrix spike samples consisted of clean sand (same sand used in column deployments and controls) that had been spiked with a known mass of explosive compound. Recovery of the spiked mass gave an indication of the extraction efficiency. In addition, a surrogate compound (1, 2-dinitrobenzene (1,2-DNB)) was added to each sample prior to extraction to determine the extraction efficiency.

3.4.6 Field Schedule for the Controlled Burn. Table 3-5 shows the field schedule that was implemented for the on-site installation, retrieval, and pre- and post-burn sampling activities in August 2004. On-site activity days are shown with shading in Table 3-5 to differentiate between activities on and off-range. On Tuesday, August 3rd, Battelle staff arrived in the field with supplies that had been loaded and driven to the site in a box truck. On Wednesday, August 4th, materials and supplies were unloaded and constructed to prepare for on-range activities. Battelle staff met with other team members and subcontractors and a meeting was held with Eglin Staff to coordinate on-site activities for the next day. Thursday, August 5th, was the first day on-range. The 4 test areas were identified and pre-burn setup commenced. Thermocouple stations were constructed and staff began spreading pine straw outside the 4 test areas. Friday, August 6th was the day of the controlled burn. Prior to burning, all pre-burn surface soil samples were collected from the 4 test areas, migration columns and test soils were installed and deployed, and the remaining pine straw was laid down in the test areas. The burn was started at 1700 via helicopter. Observations made during the burn and weather conditions prior to-, during, and after the burn are discussed in Section 4.0. A 24-hour wait period was implemented for safety purposes and staff were not permitted to access the range on Saturday, August 7th. Field Staff were permitted to access the range for post-sampling activities on Sunday, August 8th at approximately 0830 to 1200. All post-sampling activities were conducted during this time. This included sampling surface soils in the 4 test areas, collecting all test soil deployments (soil dishes, melting columns, migration columns, and soil trays), deconstructing and retrieving the thermocouple stations and obtaining the data loggers, logging all samples collected into field notebooks, and collecting digital photographs of the burn site. Field staff were permitted to return to the range on Monday, August 9th from 0800 to 1000 to install 15 surface water traps and to load the traps with sample jars. On Tuesday, August 10th, Field Staff shipped the remaining equipment back to Battelle and left Eglin AFB.

Table 3-5. Field Schedule of Events

Task	Sub-Tasks	Date							
		Tuesday	Wednesday	Thursday	Friday	Saturday	Sunday	Monday	Tuesday
		8/3/2004	8/4/2004	8/5/2004	8/6/2004	8/7/2004	8/8/2004	8/9/2004	8/10/2004
Mobilization to Site	1) team members arrive at Eglin AFB	X							
	2) unpack equipment and begin equipment assembly		X						
	3) meet w/ staff at Eglin AFB		X						
Setup	1) spread pine straw			X	X				
	2) install T-couples and data loggers (4)			X	X				
	3) install soil dishes (48)				X				
	4) install melting columns (24)				X				
	5) install migration columns (12)				X				
	6) install temp indicator strips				X				
	7) setup sample grids (4) and conduct pre-burn soil sampling				X				
Burn	1) photos/video				X				
24-Hour Cool-Down Period (Safety Requirement)						X			
Post-Burn	1) retrieve soil dishes (48)						X		
	2) retrieve melting columns (24)						X		
	3) retrieve migration columns (12)						X		
	4) retrieve temp equipment						X		
	5) conduct post-burn soil sampling at 4 grids						X		
	6) install surface water traps							X	
Demobilization from Site	1) pack up materials and leave site								X

Note – Shaded areas indicate on-range activity days. A 24-hour safety period was implemented after the burn and therefore, field staff were not permitted on the range Saturday, August 7, 2004.

4.0 RESULTS AND DISCUSSION

The results from the laboratory studies, initial site characterization, and the field-scale burn are presented and discussed in that order in the following sections.

4.1 Laboratory Thermal Decomposition Studies

4.1.1 Preliminary Examination and Test Design (TNT only). Thermal decomposition of neat TNT and 4% TNT in benzene had previously been investigated over a temperature range of 200°C to 300°C, where samples were heated in 200-μL (~2.2 mm × 60 mm) flame-sealed glass tubes, and the fraction of TNT remaining was quantified using GC/FID (Oxley et. al., 1994; Oxley et. al., 1995). To establish a baseline for the protocol used in the FERM laboratory studies, neat TNT (0.1 g) was heated in 2-mL glass ampoules at 100°C, 175°C, and 250°C, in sealed ampoules for all three temperatures and in open glass ampoules for the two higher temperatures (Table 4-1). For comparison, the rate constants from the sealed vial thermolyses and from the previous studies are shown in Figure 4-1.

Table 4-1. Kinetic Results from Heating Neat TNT in Open Versus Sealed Ampoules

Temperature °C	Sealed				Open			
	Rate Constant	t _{1/2} (min)	R ²	% decr.	Rate Constant	t _{1/2} (min)	R ²	% decr.
100	1.21E-07	95455	0.59	25				
175	3.56E-05	324	0.23	8	6.29E-04	18	0.66	45
250	1.33E-04	87	0.57	8	2.98E-03	4	0.96	60

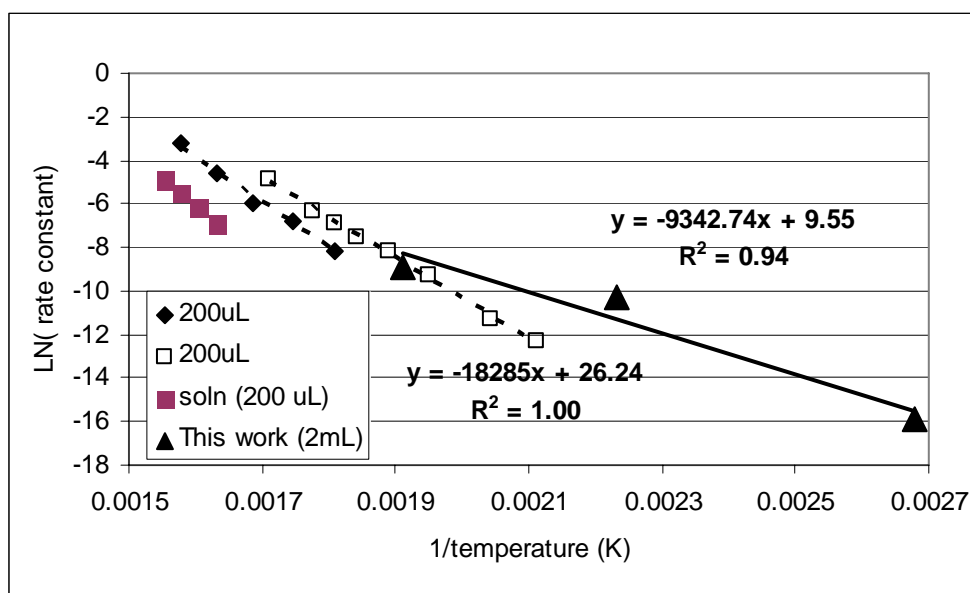


Figure 4-1. Comparison of TNT Arrhenius Plots of Previous and New Data

The decomposition rate observed in the FERM study was clearly slower than the rates previously observed. This suggested that the slower vapor-phase decomposition dominated under the experimental conditions using larger (sealed) reaction vessel volumes and smaller quantities of TNT. This observation raised the question of whether the heating of soil-bound TNT should be done in open or sealed containers. On one hand, the use of sealed containers would prevent TNT evaporation and facilitate the identification of evolved gases. However, thermolyses in sealed containers might alter the decomposition kinetics. Decomposition products might enhance or retard decomposition. Large volumes of soil might act as a diluent to mitigate any potential influence on TNT decomposition. Retention of water in the sealed vials could affect decomposition kinetics by supporting hydrolysis reactions. Another important factor to consider in using the sealed vial approach was the limited amount of oxygen within headspace and soil pores in the vial and the potential for this to limit decomposition via oxidative reactions.

To evaluate the effect of using sealed versus open reaction vessels, preliminary studies were performed using neat TNT and two contaminated soils, at two temperatures (290°C and 200°C). One soil came from a site at Sandia National Laboratory, NM and the other from a site at Eglin AFB, FL. To eliminate moisture as a potential variable, the soils were gently heated to 50°C and held for approximately 14 hours to remove moisture. The initial TNT concentrations in the soils were 126 µg of TNT per gram of Sandia soil, and 65 µg of TNT per gram of Eglin soil.

With one exception, the TNT was lost faster from the soils than from neat TNT, but decomposition trends were different between the two soils. Figures 4-2 and 4-3 show the fraction of TNT remaining in the reaction vials after 10 minutes and 60 minutes at 290°C and 200°C, respectively. At 290°C, TNT decreased faster in the soils than from the neat TNT. At this temperature TNT loss in Sandia and Eglin soils was similar in the open and sealed vials, but neat TNT loss was somewhat faster in the open vials. At 200°C the fraction of TNT decrease was notably greater from open vials than sealed for neat TNT, but in Sandia soil the opposite trend was observed.

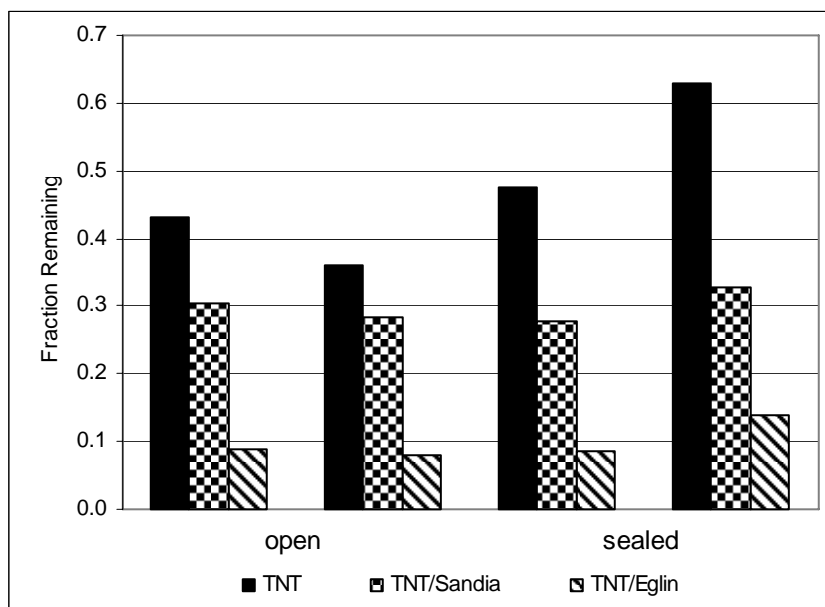


Figure 4-2. Preliminary Study: TNT Decomposition Neat and in Sandia and “old” Eglin Soils (10 min @ 290°C)

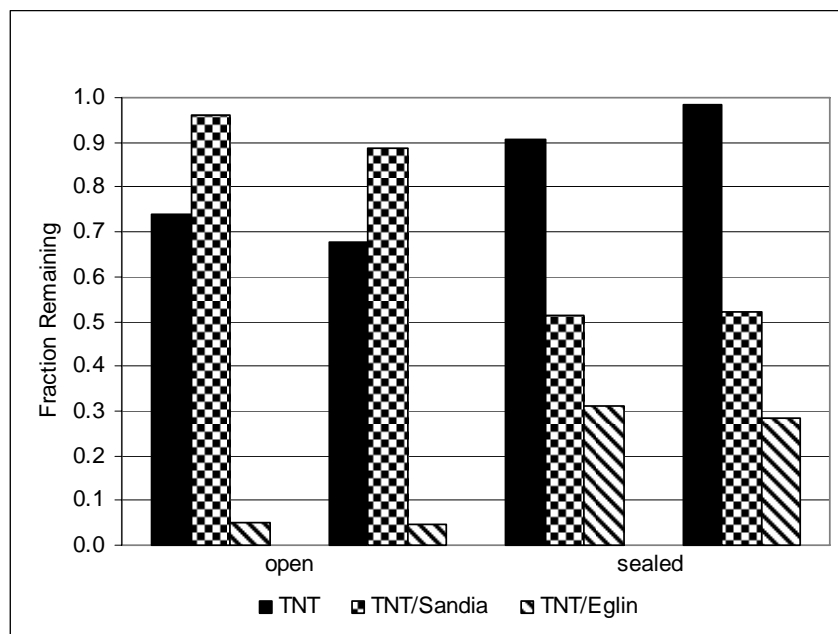


Figure 4-3. Preliminary Study: TNT Decomposition Neat and in Sandia and “old” Eglin Soils (60 min @ 200°C)

Under all conditions, the percentage of TNT decrease was greatest with the Eglin soil. To examine the effect of soil type, a further soil sample was obtained from Eglin AFB. This Eglin soil sample was different in that the original or “old” Eglin soil sampled was white beach sand and the new Eglin soil was a more loamy soil collected nearer to the FERM pilot-scale, burn site, once that site had been identified. In a further attempt to resolve the effect of open versus sealed reaction vials, TNT-contaminated silica sand was also included in an experiment. An isothermal heating test (175°C) was performed in triplicate using 2-mL reaction vials containing either neat TNT or TNT in one of the four matrices. The fractions of TNT remaining after 60 minutes of heating are shown in Figure 4-4.

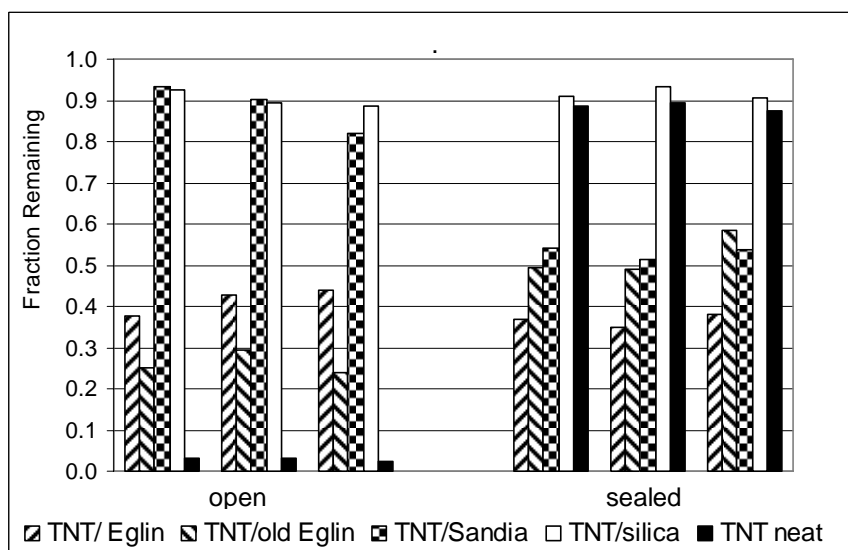


Figure 4-4. Preliminary Study: TNT Decomposition in Several Matrices (60 min @ 175°C)

At low temperatures (200 and 175°C) TNT in open vials disappeared notably faster than in sealed vials. TNT in silica disappeared at the same rate regardless whether the vials were open or sealed. The rate of TNT loss in silica coincided with that at which neat TNT decreased in the sealed vials. This was interpreted to mean that the “real” rate of TNT decomposition was observed in the sealed vials, and in the open vials evaporation became significant. Accordingly, all neat TNT samples were run in sealed reaction vials. In sealed vials, where evaporation of TNT could not be a factor, TNT in any of the soils disappeared faster than the neat TNT. Thus, soil-assisted decomposition was postulated. Evaporation of TNT from the soils in the open vials did not appear to be a large effect; subsequent migration studies (section 4.1.4) quantified it. Surprisingly, in Sandia soil, TNT loss was actually slower in open vials. This suggested that in that soil the reaction was inhibited by containment of an inhibitory reaction product.

The neat TNT decreased more in the opened vials in this experiment at 175°C than it did in the previous experiment at 200°C also heated for 1 hour. The thermolyses at 200°C were performed in open melting point tubes (1.5 to 1.8 mm i.d. × 45 mm) using ~0.4 mg TNT, while the experiments at 175°C were conducted with ~0.1 mg TNT in the same size, open vials as were used for the soil thermolyses (2-mL vials, 11.4 mm o.d. × 32 mm). The larger diameter open containers apparently enhanced evaporation/sublimation.

4.1.2 Kinetics. Explosive-contaminated soils were heated in open vials since these best simulated the modeled application (open burn). However, when it was necessary to heat neat TNT or RDX, the vials were sealed. The kinetic experiments were conducted in the Wheaton™ reaction vials heated at 100°C, 175°C, and 250°C for various lengths of time. The fraction of explosive remaining versus time was plotted to extrapolate first-order kinetic constants. Generally, the decrease was linear up to at least 50% decomposition. The first-order rate constants obtained from the slopes of the first-order plots are tabulated in Tables 4-2 for TNT and 4-3 for RDX. These constants were used to construct the Arrhenius plots shown in Figure 4-5 for TNT, Figure 4-6 for RDX, and Figure 4-7 for a comparison of TNT and RDX kinetics. The Arrhenius parameters obtained for neat RDX and 10% RDX in soil (Table 4-3) are similar to each other and to those we previously reported for the thermal decomposition of RDX neat, 1% in benzene, or 0.7% in acetone (45.4 to 37.8 kcal/mol and 7.40×10^{17} to $1.99 \times 10^{14} \text{ s}^{-1}$ in the temperature range 200°C to 250°C) (Oxley et. al., 1994b).

Figures 4-5 through 4-7 illustrate two striking observations applicable to both TNT and RDX. First, the presence of moisture in soil only slightly enhanced the decomposition of the explosive. Second, as the concentration of the explosive increased from 0.001% (10 mg/kg) to 0.1% (1000 mg/kg) to 10% (10^5 mg/kg), the decomposition of the explosive slowed, until at 10% the rate of its decomposition was close to that of the neat TNT or RDX. Compared to this concentration effect, water had little effect on explosive decomposition.

The temperature range selected for the TNT thermolyses experiments (100°C to 250°C) could not be used for RDX because RDX decomposition at 210°C was as rapid as TNT decomposition at 250°C. This reflected the lower thermal stability of RDX compared to TNT (Figure 4-7). However, the rate of decomposition of neat RDX and of 10% RDX in soil quickly decreased as the temperature was lowered below its melting point (202°C). At 100°C, RDX decomposition was so slow that it could not be quantified for comparison to the decomposition of TNT at that temperature. Only the decomposition of 0.1% RDX in soil at 100°C was rapid enough to be quantified and allow such a comparison.

Several possible explanations were considered for the observation that the most rapid decomposition occurred at the lowest, rather than at the highest, concentration of explosive. An explanation which would apply only to RDX is that the highly dispersed, low concentration RDX remained longer in the molten phase where decomposition is faster. Explanations applying only to open vials or only to closed

Table 4-2. TNT Decomposition Rates and Arrhenius Parameters

10 mg/kg TNT in Eglin Soil of 0.4% Moisture								
°C	rate constant	R ²	% dec	t _{1/2} (min)				
100	3.95E-06	0.60	91	2924				
175	1.67E-03	0.40	91	6.9				
175	1.71E-03	0.50	91	6.8				
250	1.24E-02	0.70	92	0.9				
E kcal/mol	E kJ/mol	A s ⁻¹	R ²					
21.38	89.5	2.34E+07	0.95					
1000 mg/kg TNT in Eglin Soil of 0.4% Moisture					1000 mg/kg TNT in Eglin Soil of 5% Moisture			
°C	rate constant	R ²	% dec	t _{1/2} (min)	rate constant	R ²	% dec	t _{1/2} (min)
100	2.81E-06	0.77	50	4110	3.78E-06	0.91	57	3056
175	5.02E-04	0.57	50	23	8.13E-04	0.62	67	14
175	4.82E-04	0.87	53	24	6.37E-04	0.56	60	18
250	2.87E-03	0.86	99	4.0	3.48E-03	0.98	98	3.3
250	3.10E-03	0.76	88	3.7	3.44E-03	0.83	88	3.4
E kcal/mol	E kJ/mol	A s ⁻¹	R ²		E kcal/mol	E kJ/mol	A s ⁻¹	R ²
17.59	73.6	9.75E+04	0.96		17.1	71.7	7.77E+04	0.94
100,000 mg/kg TNT in Eglin Soil of 0.4% Moisture					100,000 mg/kg TNT in Eglin Soil of 5% Moisture			
°C	rate constant	R ²	% dec	t _{1/2} (min)	rate constant	R ²	% dec	t _{1/2} (min)
100	1.14E-07	0.44	0.8	101316	1.99E-07	0.95	51	58040
175	4.95E-05	0.36	27	233	4.93E-05	1.0	15	234
175	2.76E-05	0.88	47	418	2.84E-05	0.76	67	407
250	4.42E-04	0.85	38	26	5.44E-04	0.86	51	21
E kcal/mol	E kJ/mol	A s ⁻¹	R ²		E kcal/mol	E kJ/mol	A s ⁻¹	R ²
21.76	91.1	9.54E+05	0.97		16.6	69.5	4.78E+03	0.97
Neat TNT in Sealed Vials					Neat TNT in Open Vials			
°C	rate constant	R ²	% dec	t _{1/2} (min)	rate constant	R ²	% dec	t _{1/2} (min)
100	1.21E-07	0.59	25	95455				
175	2.03E-05	0.93	42	569	6.29E-04	0.66	45	18
250	1.33E-04	0.57	8	87	2.98E-03	0.96	60	4
E kcal/mol	E kJ/mol	A s ⁻¹	R ²					
18.39	77.0	9.60E+03	0.97					

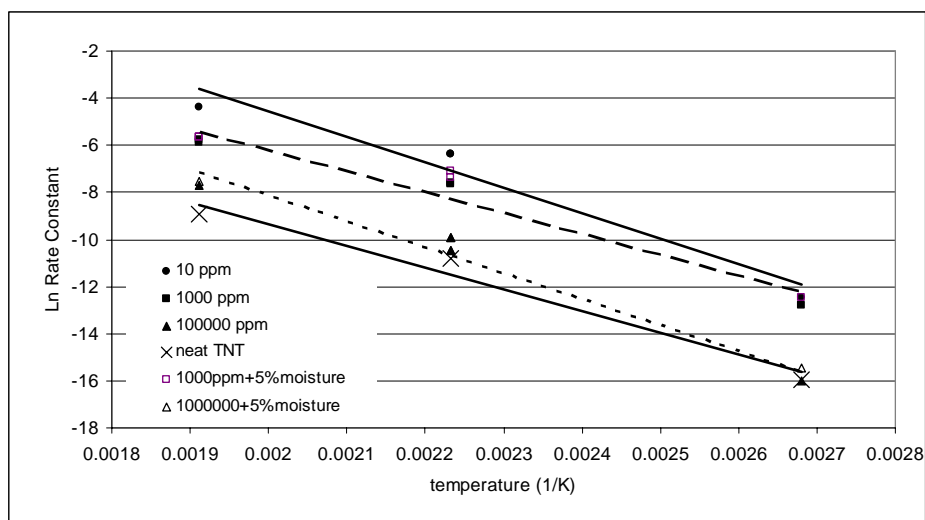


Figure 4-5. Arrhenius Plots of TNT Decomposition

Table 4-3. RDX Decomposition Rates and Arrhenius Parameters

1000 mg/kg RDX in Eglin Soil of 0.4% Moisture					1000 mg/kg RDX in Eglin Soil of 5% Moisture			
°C	rate constant	R ²	% dec	t _{1/2} (min)	rate constant	R ²	% dec	t _{1/2} (min)
100	8.90E-05	0.85	60	130				
175	2.12E-03	0.66	58	5.4	1.95E-03	0.88	57	5.9
190	2.57E-03	0.87	71	4.5	2.65E-03	0.84	69	4.4
210	2.68E-03	0.97	41	4.3	2.32E-03	0.88	34	5.0
E kcal/mol	E kJ/mol	A s ⁻¹	R ²					
11.9	49.9	9.63E+02	0.97					
100,000 mg/kg RDX in Eglin Soil of 0.4% Moisture					100,000 mg/kg RDX in Eglin Soil of 5% Moisture			
°C	rate constant	R ²	% dec	t _{1/2} (min)	rate constant	R ²	% dec	t _{1/2} (min)
175	1.86E-05	0.80	90	621	2.04E-05	0.94	90	566
190	5.96E-05	0.88	54	194	6.35E-05	0.84	64	182
210	4.60E-04	0.62	54	25	8.56E-04	0.78	81	13
E kcal/mol	E kJ/mol	A s ⁻¹	R ²		E kcal/mol	E kJ/mol	A s ⁻¹	R ²
39.6	166	3.68E+14	0.99		46.4	194	7.00E+17	0.97
Neat RDX in Sealed Vials								
°C	rate constant	R ²	% dec	t _{1/2} (min)				
175	3.01E-05	0.95	44	384				
190	3.75E-04	0.93	42	31				
210	1.03E-03	0.55	43	11				
E kcal/mol	E kJ/mol	A s ⁻¹	R ²					
42.7	179	2.88E+16	0.91					

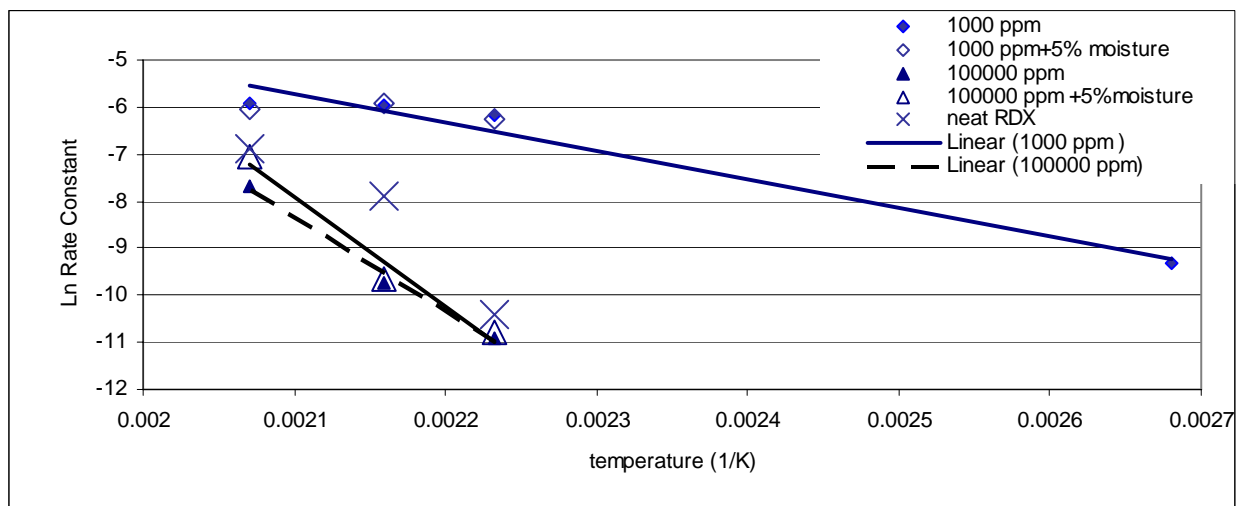


Figure 4-6. Arrhenius Plots of RDX Decomposition

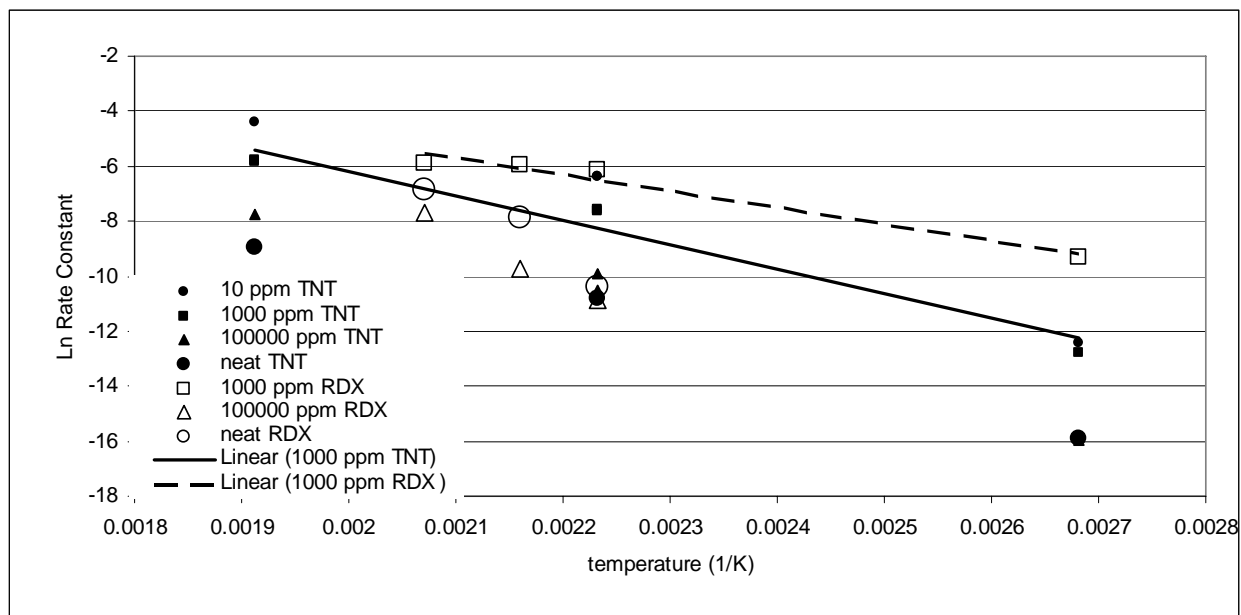


Figure 4-7. Arrhenius Plots: RDX and TNT Decomposition Neat and in Eglin Soil (with 0.4% Moisture)

vials may include that increased evaporation of the dilute explosive (open vials) or high concentration of explosives in sealed vials build up a retarding species or deplete the limited oxygen supply. Indeed, side-by-side comparisons of open and sealed reaction vials with 0.01% RDX in soil showed the RDX in the sealed tube decomposed more slowly, at ~50% of the rate observed in the open vial (0.0012 s^{-1} vs. 0.0021 s^{-1}); but this will not explain the factor of 100 difference between the rate of the 0.1% and 10% RDX.

A possible explanation, which would apply to all cases, is enhanced soil-explosive interactions at low concentrations of explosive. Assuming that at a high explosive concentration, the percentage of explosive surface in contact with the soil is smaller than at low explosive concentration, decomposition associated with a soil surface mechanism is minor at high explosive concentrations compared to the mechanism associated with neat explosive decomposition. This would explain the reason that decomposition rates of 10% explosive in soil were similar to those of the neat explosive.

4.1.3 Decomposition Gases. Decomposition gases from neat and soil-phase TNT and RDX were examined by heating the materials at 250°C in sealed glass-capillary tubes. GC/TCD analyses showed five and sometimes six peaks. Four peaks were identified and quantified using authentic standards as N_2 , CO , CO_2 , and N_2O , and a fifth was identified as water but not quantified. For both TNT and RDX in soil, another small peak sometimes appeared and was identified as NO based on GC/MS analysis. The amount of gas released from the samples of 0.1% RDX or 0.1% TNT in soil was so small that accurate quantification was not possible, though it was evident the same gases were formed as in the higher explosives concentration. Because the samples were sealed under air, samples with only 0.1% explosive showed large backgrounds of nitrogen skewing the results; thus, only one of these samples is reported in Table 4-4. RDX, having a better oxygen balance than TNT, produced significantly more gas—approximately 4 moles gas per mole RDX, while TNT produced less than 2 moles gas per mole.

Table 4-4. Cumulative Decomposition Gases from Neat and Soil-Bound Explosives at 250°C

TNT										
TNT Conc.	Time	mol N ₂ /mol explosive	stdev	mol CO ₂ /mol explosive	stdev	mol CO/mol explosive	stdev	mol N ₂ O/mol explosive	stdev	Sum of all gases
Neat	4 hour	0.26	0.05	0.30	0.03	0.03	0.00	--	--	0.59
	16 hour	0.62	0.03	1.08	0.06	0.09	0.01	--	--	1.79
10%	2 hour	0.44	0.04	0.58	0.08	0.06	0.00	--	--	1.08
	41 hour	0.51	0.02	1.08	0.04	0.05	0.01	--	--	1.64
0.1%	24 hour	1.30	0.41	0.81	0.07	0.04	0.04	--	--	2.16
RDX										
RDX Conc.	Time	mol N ₂ /mol explosive	stdev	mol CO ₂ /mol explosive	stdev	mol CO/mol explosive	stdev	mol N ₂ O/mol explosive	stdev	Sum of all gases
Neat	5 min	1.6	0.06	0.84	0.05	0.72	0.02	1.12	0.01	4.27
	58 hour	1.6	0.06	0.88	0.05	0.73	0.04	1.18	0.03	4.34
10%	5 min	1.1	0.13	0.98	0.07	0.28	0.04	1.12	0.09	3.46
	58 hour	1.5	0.51	0.83	0.31	0.21	0.06	0.03	0.02	2.52

TNT and RDX decomposition gases are shown in Table 4-4. RDX decomposition at 250°C was complete within 5 minutes after which time the data remained constant through the duration of the experiment. Figure 4-8 plots the time series evolution of TNT decomposition from 10% TNT in soil. The presence of soil did not alter the TNT decomposition gases in terms of composition or amount. Figure 4-9 shows the evolution of CO₂, the most abundant TNT decomposition gas, for varying TNT concentrations in soil. In contrast, there were two notable differences between the decomposition gases of neat RDX and that of RDX in soil. The production of N₂O appeared to be lower in the soil (58 hour data) than the neat RDX. CO production also appeared inhibited when comparing the data for neat RDX to that of RDX/soil samples.

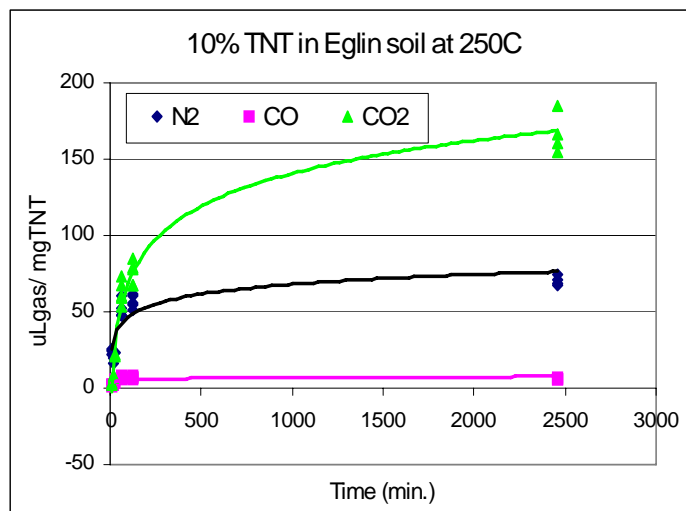


Figure 4-8. Evolution of Decomposition Gases from 10% TNT in Soil at 250°C

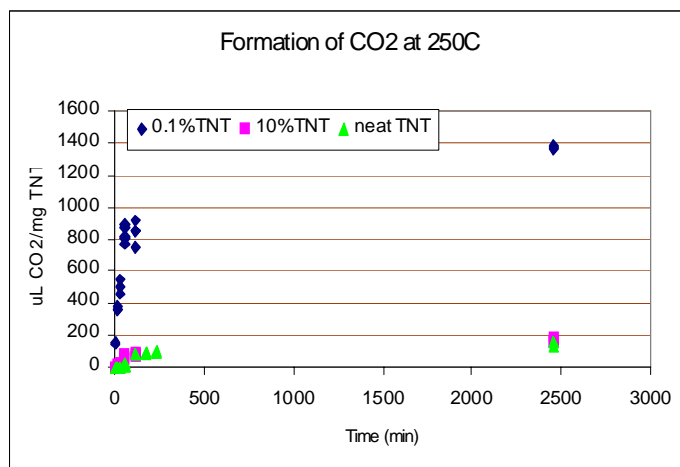


Figure 4-9. CO₂ Production During TNT Decomposition at 250°C

Production of organic gases from the decomposition of TNT and RDX was examined using GC/MS. For TNT, no new organic species were observed. For RDX, small organic molecules including methanol, methyl formate, and dimethylnitrosoamine were detected. These gases were reported from previous experiments that examined degradation of RDX in soil. Acetone and acetonitrile were detected and attributed to contamination of the glassware since these were observed in both the decomposition of neat RDX and RDX in soil (Jenkins et. al., 2000a). The detection of trimethylamine was unexpected but confirmed with authentic samples.

4.1.4 Migration Studies. Column experiments were conducted to investigate the potential for heat induced migration of residual TNT or RDX into the soil profile during the controlled burn. The column setup included two layers of soil, a top layer of explosive-contaminated soil (10%) and a bottom layer of clean soil. Two experimental approaches were used. The first heated the entire length of the column that contained TNT-contaminated soil to 250°C to avoid developing a thermal gradient in the soil.

During heating, a black residue, presumably TNT and/or products associated with TNT decomposition, was found along the length of the empty column above the TNT-contaminated soil layer and above the heat-tape wrapping. This residue was not a result of TNT contamination of the glass column during loading because an inner tube had been used to channel the soil into place. It appeared that the black residue along the empty column above the soil was the result of TNT sublimation. Surprisingly, this residue was not observed when silica was used rather than soil. These observations need to be considered in conjunction with observations summarized in Figure 4-10. From observations made in the earlier discussed experiments, it was assumed that the difference between the loss of TNT from open vials of neat TNT versus open vials of TNT-contaminated soil or silica was that the TNT in the soil matrix did not sublime, while the neat TNT did. This is not exactly the case. The presence of black residue along the length of the empty column above the contaminated soil indicated that TNT did sublime from the soil. The extent of TNT sublimation was quantified in several experiments that are summarized in Table 4-5.

In the second experimental configuration, only the portion of the column containing contaminated soil was wrapped in heating tape. Following heating, soil was removed in 1-cm sections starting from the initially clean soil at the bottom (area where *melted* TNT or RDX would migrate) to the interface of the contaminated soil (where *remaining* TNT or RDX would be) to the contaminated soil/empty column interface (where TNT or RDX which *sublimed* would be found). Each centimeter of soil was extracted

with acetonitrile, and explosive content was quantified. The empty section of column was examined as three 9-cm long segments. Figure 4-10 shows a typical migration experiment. Results for the TNT and RDX experiment are summarized in Tables 4-5 and 4-6, respectively. In most cases, more than 99% of the RDX was decomposed and did not appear in soil segments nor fragments or on the glass column. This is a higher percentage decomposition than was observed for TNT. In general, less than 1% of the RDX was observed for our experimental conditions in the empty column above the contaminated soil. This can be compared to the more volatile TNT for which 2% to 8% was found in the column headspace. This migration is the result of sublimation.

In addition to analyzing the acetonitrile soil extracts to quantify RDX or TNT present, the extracts were introduced into a GC/MS to identify other condensed-phase decomposition products. Figure 4-11 shows the GC/MS chromatograms obtained for several sections of the soil in the TNT migration study. Some of the more prominent peaks were observed on the contaminated soil/air interface (TNTMIG17L10). Computer matching suggested these peaks were TNT, 1, 2-benzenedicarboxylic acid, and mono(2-ethylhexyl ester). The latter is not a TNT decomposition product; rather it was present in the soil prior to heating (see time-zero chromatogram in Figure 4-12). Most of the other species are probably indigenous to the soil, though they are too minor to appear in the time-zero chromatogram (Figure 4-12). Dinitrotoluenes were readily observed in the soil after heating TNT.

empty, unheated tube		mg TNT	
		0.009	
		0.011	
soil with 10% TNT, heated ~250C, 3h			Decomposition ~84%
		5.55	2.2%
		0.116	
		0.007	
		0.005	
		0.048	
clean soil, unheated		16.96	6.9%
		18.81	
		0.153	
		0	
		0	7.6%

Figure 4-10. Experimental Setup and Results for a TNT Migration Experiment

Table 4-5. Summary of TNT Migration Results after Heating at 250°C

Test #	Treatment Duration (hrs @250°C)	TNT _{initial} (mg)	Sublimed		Remaining		Melted		% TNT Decrease	Soil
			TNT (mg)	%	TNT (mg)	%	TNT (mg)	%		
1	6	267	18.3	7	6.9	3	32.1	12	78	Eglin
2		300	6.1	2	10.1	3	41.0	14	81	Sandia
1	3	271	3.7	1	8.8	3	37.6	14	82	Eglin
2		271	9.2	3	2.0	1	22.6	8	88	Eglin
3		254	5.6	2	17.1	7	19.0	7	84	Eglin
1	1	254	5.9	2	19.2	8	22.9	9	81	Eglin
2		257	19.4	8	7.5	3	25.0	10	79	Eglin

Table 4-6. Summary of RDX Migration Results after Heating at Multiple Temperatures

Test #	Temp °C	Hours	RDX _{initial} (mg)	Sublimed		Remaining		Melted		% RDX Decrease
				mg RDX	%	mg RDX	%	mg RDX	%	
1	250	3	325	1.4	0.4	0	0	0	0	99.6
3	250	1	322	1.5	0.5	1.4	0.4	7.3	2.3	96.8
4	210	3	301	0.4	0.1	0	0	0	0	99.9
5	180	3	301	0.8	0.3	239	79.5	3.4	1.1	19.1
6	200	3	301	0.03	0.0	17.7	5.9	4.2	1.4	92.7

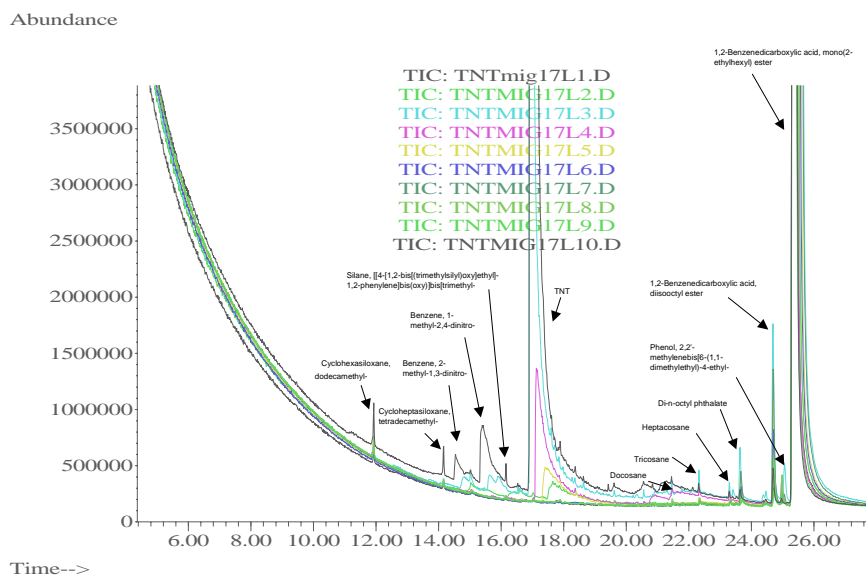


Figure 4-11. Fractions of Soil after Heating for 3 Hours at 250°C

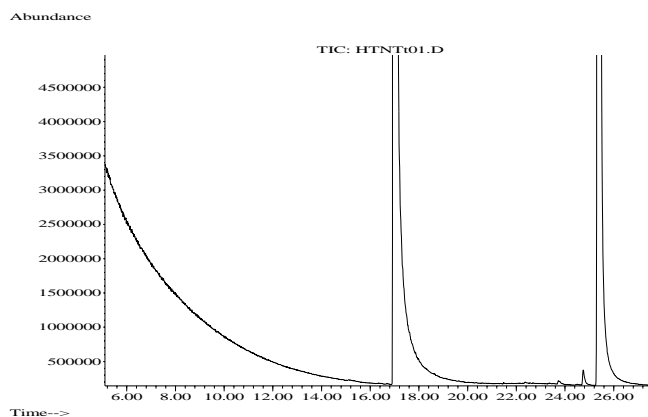


Figure 4-12. Soil with TNT (10%) Prior to Heating (Time-Zero)

Figure 4-13 is a chromatogram from GC/MS analysis of the top 1 cm of the RDX-contaminated soil after it was heated at 250°C for 3 hours. The analysis showed a number of analytes that appeared to be organic decomposition products of RDX rather than species associated with the soil. None of the compounds could be matched to the GC/MS computer library. It was assumed that the mono-, di- and tri-nitroso analogs of RDX were among the compounds detected since they have been observed in the thermolysis of neat RDX and the degradation products of RDX in soil (Pennington, 1989; Oxley et. al., 1994b).

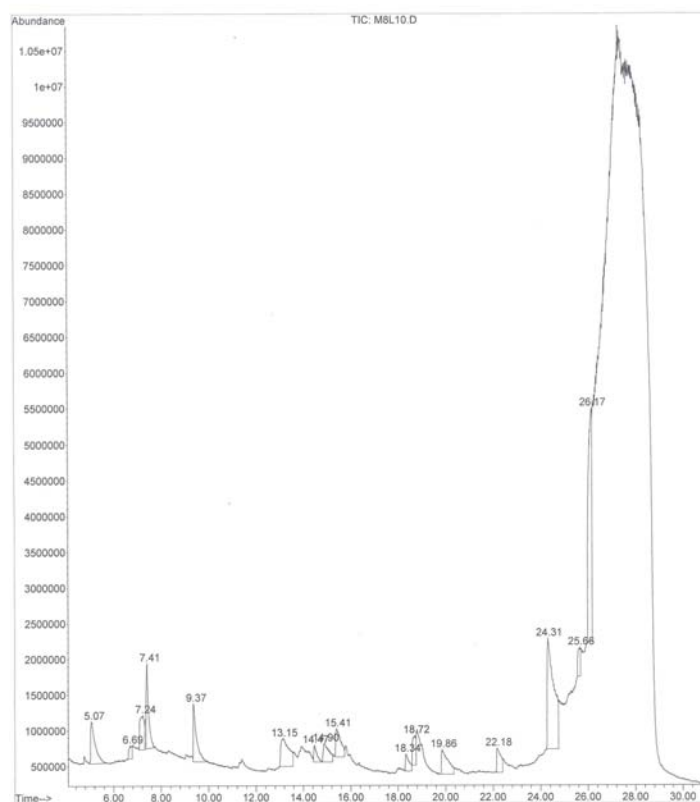


Figure 4-13. GC/MS Chromatogram of the Top 1-cm of Soil in RDX Migration Study

4.2 Initial Site Characterization

4.2.1 Soil Concentrations. Figure 4-14 shows the distribution of the highest concentrations for TNT, RDX, HMX, and nitroglycerine (NG) at each grid segment and quadrant sampled during the initial C52-N characterization effort (background sample location not shown). The highest concentrations observed for the four explosives (i.e., TNT, RDX, HMX and NG) for each sampling area are provided in Table 4-7. The data show energetic residuals ranged into the low parts per million concentration in all five sampled areas. As expected, the concentrations for all 4 explosives were below the detection level of 0.2 mg/kg in the control area.

The explosive residuals concentrations were spread heterogeneously across the site and within the test areas. At Site 1 and 2, HMX was the predominant surface compound, appearing at low mg/kg levels in virtually every soil sample composite. The highest HMX level detected was at Site 1 and was 3.52 mg/kg, followed by RDX and TNT at 2.03 and 10.1 mg/kg, HMX, respectively. Site 2 resulted in slightly less surface energetic residual, but also contained predominantly RDX followed by HMX and TNT, respectively.

4.2.2 Plant Tissue and Surface Concentrations. Eight plant species were identified and sampled from Site 1, 2, and 3 and processed for surface and in-tissue explosive residual analysis. Tables 4-8 through 4-12 show the residual concentrations on the plant surfaces and inside plant tissue along with the explosives concentrations from the soil samples collected in close proximity to the location of the sampled plant.

Table 4-7. Highest Concentrations of Energetic Concentrations Detected in Surface Soils During the Initial Site Characterization

Sample Area	Compound and Concentration (mg/kg)			
	TNT	RDX	HMX	NG
Site 1 – Target Impact Area (North)	10.1	2.03	3.52	3.00
Site 2 – Target Impact Area (South)	1.03	6.05	19.5	0.840
Site 3 – Plateau Area	0.098	0.619	0.106	0.047
Site 4 – Control Area ^(a)	<0.20	<0.20	<0.20	<0.20
Site 5 – Washout Bed	1.59	1.53	0.184	0.340
Site 6 – Blowhole	1.30	0.158	0.096	0.240

(a) 0.20 ppm = lower detection limit.

The most abundant plant species found at C52-N was *Andropogon virginicus*. A total of 17 samples of this plant were collected for analysis. Two tissue samples from this plant showed elevated in-tissue concentrations of TNT and one sample had detectable concentrations of RDX on the plant surface. There was no direct correlation between soil concentration and plant tissue concentration for TNT. Coupling this with the lack of detection in the majority of the plant samples made it impossible to draw any conclusion of this plant's ability to uptake and/or transform explosives residuals.

Eupatorium compositifolium from Site 1 showed detectable concentrations of HMX and RDX in their tissue, RDX on their surface, and no detectable concentrations of TNT. On average, Site 2 samples showed higher RDX concentrations both on and in the plant tissue, low mg/kg concentrations of TNT were detected in 3 of the 5 samples, and no HMX associated with any of the *Eupatorium compositifolium* samples. The higher concentrations (per mass basis) of RDX and TNT found in this plant's tissues

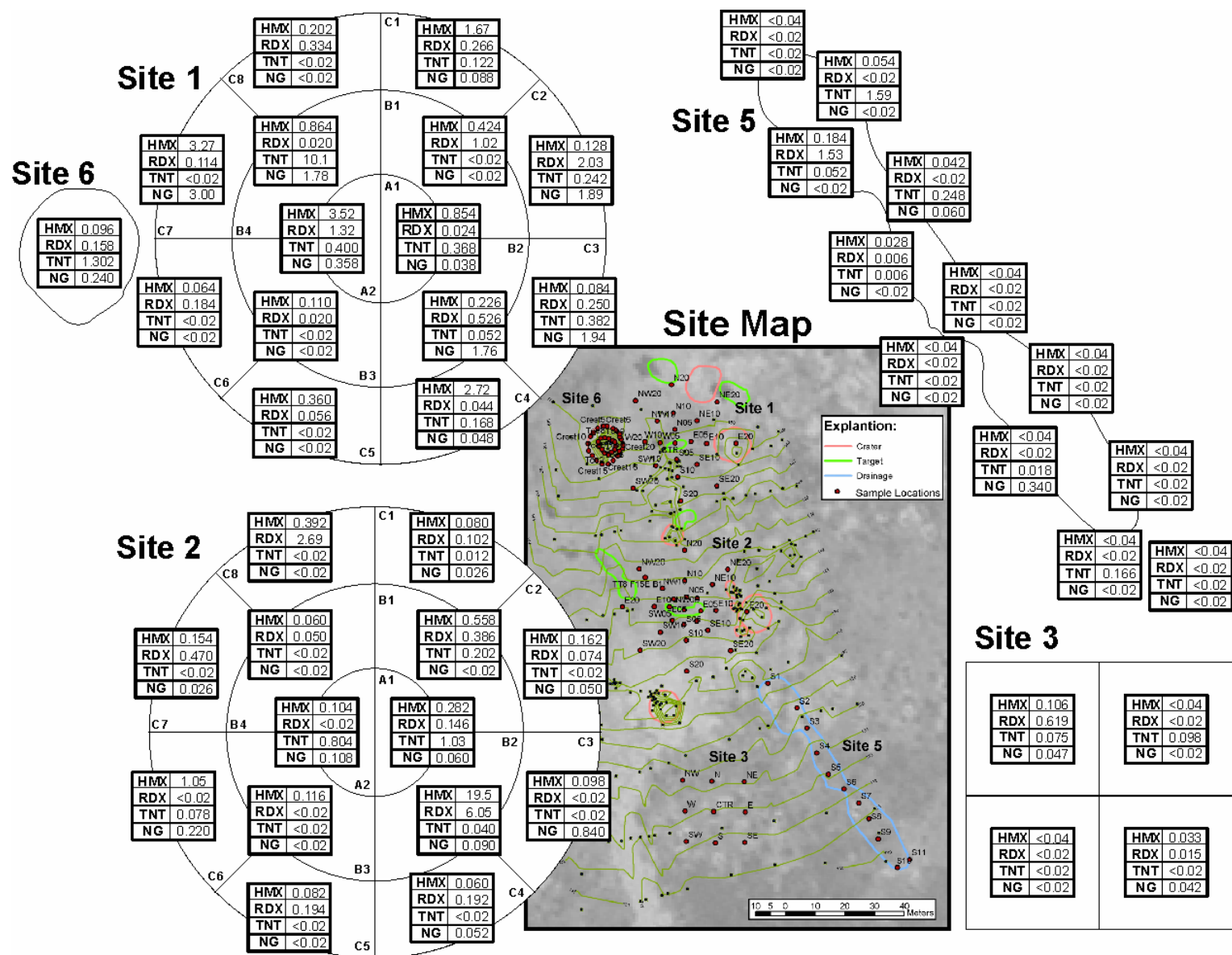


Figure 4-14. Initial Site Characterization Sampling Results at Cat's Eye, C52-N, Eglin AFB (Background Location not Shown)

Table 4-8. Results of Concentration of Explosive Compounds in Surface Soil, On Plant Tissue^(a), and In Plant Tissue at Site 1 (Target Impact Area), C52-N, Eglin AFB

Soil or Plant Type	Grid Segment	Concentration of Explosives in Surface Soil, On Plant Surface and In Plant Tissue (mg/kg)														
		HMX	RDX	TNT	2,4 DNT ^(b)	2,6 DNT	1,3,5 TNB	1,3,-DNB	2- ADNT ^(b)	4-ADNT	2-NT	4-NT	3-NT	NB	Tetryl	NG
Soil	A1	0.85	0.02	0.37	<0.02	<0.02	<0.02	<0.02	0.02	0.014	NA	NA	NA	NA	<0.02	0.04
Soil	A1 (FD)	0.09	0.02	4.79	<0.02	<0.02	0.01	<0.02	0.03	0.024	NA	NA	NA	NA	<0.02	0.02
<i>Andropogon virginicus</i> (Broom Sedge)	A1	<0.50	<0.50	<0.25	<0.25		0.45	<0.25	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
<i>Andropogon virginicus</i>	A1	<0.50	<0.50	<0.25	<0.25		0.65	<0.25	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
Soil	A2	3.52	1.32	0.40	0.10	0.008	<0.02	<0.02	0.02	0.026	NA	NA	NA	NA	<0.02	0.36
Soil	B1	0.42	1.02	0.01	<0.02	<0.02	<0.02	<0.02	0.01	0.010	NA	NA	NA	NA	<0.02	<0.02
Soil	B2	0.23	0.526	0.05	0.02	<0.02	<0.02	<0.02	0.02	0.020	NA	NA	NA	NA	<0.02	1.76
<i>Eupatorium compositifolium</i> (Dog Fennel)	B2	1.21	3.0 (1.0)	<0.25	<0.25		0.54	<0.25 (2.76)	0.66		<0.25 (15.8)	<0.25	5.95 (1.18)	<0.25	NA	NA
<i>Yucca flaccida</i>	B2	<0.50	0.59	<0.25	<0.25	<0.25	1.03	<0.25	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
“Lawn Grass”	B2	<0.50	<0.50 (0.76)	2.03	<0.25	<0.25	0.41	<0.25	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
Soil	B3	0.11	0.020	<0.02	0.01	<0.02	<0.02	<0.02	0.01	0.006	NA	NA	NA	NA	<0.02	0.004
Soil	B3 (FD)	0.09	0.004	0.01	<0.02	<0.02	<0.02	<0.02	<0.02	0.004	NA	NA	NA	NA	<0.02	<0.02
Soil	B4	0.86	0.020	10.1	0.03	0.004	0.03	<0.02	0.04	0.036	NA	NA	NA	NA	<0.02	1.78
Soil	C1	1.67	0.266	0.12	<0.02	<0.02	<0.02	<0.02	0.02	0.012	NA	NA	NA	NA	<0.02	0.09
Soil	C1 (LD)	1.51	0.240	0.09	<0.02	<0.02	<0.02	<0.02	0.01	0.010	NA	NA	NA	NA	<0.02	0.05
<i>Battisia lanceolata</i>	C1	<0.50	<0.50	<0.25	<0.25	<0.25	0.47	<0.25	<0.25		<0.25	<0.25 (3.73)	<1.0	<0.25	NA	NA
Soil	C2	0.13	2.03	0.24	0.01	<0.02	<0.02	<0.02	0.01	0.016	NA	NA	NA	NA	<0.02	1.89
<i>Andropogon virginicus</i>	C2	<0.50	<0.50	1.28	<0.25		0.53	0.61	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
<i>Andropogon virginicus</i>	C2	<0.50	<0.50	<0.25	<0.25		0.32	<0.25	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
Soil	C3	0.08	0.25	0.38	0.02	<0.02	<0.02	<0.02	<0.02	0.02	NA	NA	NA	NA	<0.02	1.94
Soil	C3 (FD)	0.25	0.20	0.65	0.03	0.002	<0.02	<0.02	0.03	0.03	NA	NA	NA	NA	<0.02	5.54
Soil	C4	2.72	0.04	0.17	0.01	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	0.05
Soil	C5	0.36	0.06	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	<0.02
Soil	C5 (FD)	0.26	0.05	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	0.05
Soil	C6	0.06	0.18	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.004	NA	NA	NA	NA	<0.02	<0.02
Gaylussacia/Saccia (Huckleberry)	C6	<0.50	<0.50	<0.25	<0.25		0.62	<0.25	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
Soil	C7	3.27	0.11	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	3.00
Soil	C8	0.20	0.33	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	<0.02
Soil	C8 (LD)	0.18	0.34	0.002	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	<0.02
<i>Andropogon virginicus</i>	C8	<0.50	<0.50 (2.25)	4.38	<0.25		0.52	<0.25	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA

(a) Plant surface explosive residue concentrations are shown in parentheses.
(b) 2,4-DNT and 2,6-DNT isomers and 2-ADNT and 4-ADNT isomers were not resolved in plant analysis.
LD = Laboratory duplicate.
FD = Field duplicate.

Table 4-9. Results of Concentration of Explosive Compounds in Surface Soil, On Plant Tissue^(a), and In Plant Tissue at Site 2 (Target Impact Area), C52-N, Eglin AFB

Soil or Plant Species	Grid Segment	Concentration of Explosives in Surface Soil, On Plant Surface and In Plant Tissue (mg/kg)														
		HMX	RDX	TNT	2,4 DNT ^(b)	2,6 DNT	1,3,5 TNB	1,3,-DNB	2- ADNT ^(b)	4-ADNT	2-NT	4-NT	3-NT	NB	Tetryl	NG
Soil	A1	0.28	0.15	1.03	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	0.06
<i>Eupatorium compositifolium</i>	A1	<0.50 (15.4)	2.8	<0.25	0.32		0.43 (5.95)	<0.25 (5.87)	0.77		0.65 (14.9)	12.2	<1.0	<0.25	NA	NA
Soil	A2	0.10	<0.02	0.80	<0.02	<0.02	<0.02	<0.02	0.03	<0.02	NA	NA	NA	NA	<0.02	0.11
Soil	A2 (FD)	0.28	<0.02	1.74	<0.02	<0.02	<0.02	<0.02	0.04	0.04	NA	NA	NA	NA	<0.02	<0.02
<i>Eupatorium compositifolium</i>	A2	<0.50	<0.50	<0.25	<0.25		0.44	<0.25 (10.8)	<0.25		2.03 (35.4)	9.88	<1.0	(43.2)	NA	NA
<i>Eupatorium compositifolium</i>	A2	<0.50	6.55 (5.32)	6.85	0.62		0.26	0.66	2.79		<0.25	19.4	6.41	(32.2)	NA	NA
Soil	B1	0.56	0.39	0.20	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	<0.02
Soil	B2	19.50	6.05	0.04	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	0.09
<i>Eupatorium compositifolium</i>	B2	<0.50	3.98 (5.41)	1.72	0.53		0.3	0.36	5.57		2.31 (5.53)	5.73	<1.0	(5.43)	NA	NA
Soil	B3	0.12	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.03	0.03	NA	NA	NA	NA	<0.02	<0.02
Soil	B3 (LD)	0.08	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.03	<0.02	NA	NA	NA	NA	<0.02	0.07
Soil	B3 (FD)	0.09	0.09	0.06	<0.02	<0.02	<0.02	<0.02	0.03	0.03	NA	NA	NA	NA	<0.02	<0.02
<i>Eupatorium compositifolium</i>	B3	<0.50	2.22 (2.90)	3.38	0.5		<0.25	0.49 (1.34)	1.67		7.41 (4.84)	6.81	<1.0	(6.24)	NA	NA
Soil	B4	0.06	0.05	<d	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	<0.02
Soil	C1	0.08	0.10	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	0.03
Soil	C2	0.16	0.07	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	0.05
Soil	C3	0.10	<0.02	<d	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	0.84
<i>Yucca flaccida</i>	C3	<0.50	<0.50	<0.25	<0.25		<0.25	<0.25	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
Soil	C4	0.06	0.19	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	0.05
<i>Andropogon virginicus</i>	C4	<0.50	<0.50	<0.25	<0.25		<0.25	0.62	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
Soil	C5	0.08	0.19	<d	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	<0.02
Soil	C6	1.05	<0.02	0.08	<0.02	<0.02	<0.02	<0.02	0.02	<0.02	NA	NA	NA	NA	<0.02	0.22
Soil	C6 (FD)	0.06	0.11	<0.02	<0.02	<0.02	<0.02	<0.02	0.02	<0.02	NA	NA	NA	NA	<0.02	<0.02
<i>Andropogon virginicus</i>	C6	<0.50	<0.50	<0.25	<0.25		0.33	<0.25	<0.25		<0.25 (0.49)	0.89 (4.32)	<1.0	<0.25	NA	NA
Soil	C7	0.15	0.47	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	0.03
Soil	C7 (LD)	0.25	0.47	<0.02	0.08	0.00	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	1.90
Soil	C7 (FD)	0.59	0.03	<0.02	0.03	0.00	<0.02	<0.02	0.03	0.03	NA	NA	NA	NA	<0.02	0.72
Soil	C8	0.39	2.69	<0.02	<0.02	0.01	<0.02	<0.02	0.02	<0.02	NA	NA	NA	NA	<0.02	<0.02

(a) Plant surface explosive residue concentrations are shown in parentheses.

(b) 2,4-DNT and 2,6-DNT isomers and 2-ADNT and 4-ADNT isomers were not resolved in plant analysis.

LD = Laboratory duplicate.

FD = Field duplicate.

Table 4-10. Results of Concentration of Explosive Compounds in Surface Soil, On Plant Tissue^(a), and In Plant Tissue at Site 3 (Plateau Area-South End of Site), C52-N, Eglin AFB

Soil or Plant Type	Quadrant Sample Location	Concentration of Explosives in Surface Soil, On Plant Surface and In Plant Tissue (mg/kg)														
		HMX	RDX	TNT	2,4 DNT ^(b)	2,6 DNT	1,3,5 TNB	1,3,-DNB	2-ADNT ^(b)	4-ADNT	2-NT	4-NT	3-NT	NB	Tetryl	NG
Soil	Q1	0.250	1.74	0.208	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	NA	NA	NA	NA	< 0.02	0.042
Soil	Q1	0.052	0.108	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	0.020	< 0.02	NA	NA	NA	NA	< 0.02	< 0.02
Soil	Q1	<0.04	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	NA	NA	NA	NA	< 0.02	0.052
<i>Andropogon virginicus</i>	Q1	<0.50	<0.50	<0.25	<0.25		0.45	<0.25	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
<i>Quercus geminta</i> (Sand Live Oak)	Q1	<0.50	<0.50	<0.25	<0.25		0.59	<0.25	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
<i>Andropogon virginicus</i>	Q1	<0.50	<0.50	<0.25	<0.25		0.42	<0.25	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
Soil	Q2	<0.04	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	NA	NA	NA	NA	< 0.02	< 0.02
Soil	Q2	<0.04	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	NA	NA	NA	NA	< 0.02	< 0.02
Soil	Q2	<0.04	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	NA	NA	NA	NA	< 0.02	< 0.02
Soil	Q2 (LD)	<0.04	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	NA	NA	NA	NA	< 0.02	< 0.02
<i>Andropogon virginicus</i>	Q2	<0.50	<0.50	<0.25	<0.25		0.94	<0.25	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
<i>Andropogon virginicus</i>	Q2	<0.50	<0.50	<0.25	<0.25		0.57	0.47	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
<i>Andropogon virginicus</i>	Q2	<0.50	<0.50	<0.25	<0.25		0.42	1.81	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
Soil	Q3	<0.04	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	NA	NA	NA	NA	< 0.02	< 0.02
Soil	Q3	<0.04	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	NA	NA	NA	NA	< 0.02	< 0.02
Soil	Q3	<0.04	< 0.02	< 0.02	0.020	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	NA	NA	NA	NA	< 0.02	< 0.02
<i>Andropogon virginicus</i>	Q3	<0.50	<0.50	<0.25	<0.25		0.31	<0.25	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
<i>Andropogon virginicus</i>	Q3	<0.50	<0.50	<0.25	<0.25		1.15	<0.25	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
<i>Andropogon virginicus</i>	Q3	<0.50	<0.50	<0.25	<0.25		0.75	<0.25 (0.54)	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
Soil	Q4	<0.04	0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	NA	NA	NA	NA	< 0.02	< 0.02
Soil	Q4	<0.04	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	NA	NA	NA	NA	< 0.02	< 0.02
Soil	Q4	0.072	0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	NA	NA	NA	NA	< 0.02	0.042
<i>Diosperus virginiana</i> (Persimon)	Q4	<0.50	<0.50	<0.25	<0.25		0.39	<0.25	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
<i>Andropogon virginicus</i>	Q4	<0.50	0.78	<0.25	<0.25		1.17	<0.25	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA
<i>Andropogon virginicus</i>	Q4	<0.50	<0.50	<0.25	<0.25		0.64	<0.25	<0.25		<0.25	<0.25	<1.0	<0.25	NA	NA

(a) Plant surface explosive residue concentrations are shown in parentheses.

(b) 2,4-DNT and 2,6-DNT isomers and 2-ADNT and 4-ADNT isomers were not resolved in plant analysis.

LD = Laboratory duplicate.

Table 4-11. Results of Concentration of Explosive in Surface Soil at Site 5 (“Wash-Out” Bed), C52-N, Eglin AFB

Sample ID Along Transect	Concentration of Explosives in Surface Soil (mg/kg)														
	HMX	RDX	TNT	2,4 DNT	2,6 DNT	1,3,5 TNB	1,3,-DNB	2- ADNT	4-ADNT	2-NT	4-NT	3-NT	NB	Tetryl	NG
1	<0.04	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	<0.02
2	0.05	<0.02	1.59	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	<0.02
2 (LD)	0.06	<0.02	1.60	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	<0.02
3	0.18	1.53	0.05	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	<0.02
4	0.04	<0.02	0.25	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.03	0.06
5	<0.04	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.02	0.02	NA	NA	NA	NA	<0.04	<0.02
6	<0.04	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.05	<0.02
7	<0.04	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.06	<0.02
8	<0.04	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.07	<0.02
9	<0.04	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.08	0.34
9 (LD)	<0.04	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.09	0.06
10	<0.04	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.10	<0.02
11	<0.04	<0.02	0.17	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.11	<0.02
12	<0.04	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.12	<0.02

LD = Laboratory duplicate.

Table 4-12. Results of Concentration of Explosive in Surface Soil at Site 6 (“Blowhole”) and Water Samples from the South Stream, C52-N, Eglin AFB

Sample Location in Blowhole	Concentration of Explosives in Surface Soil (mg/kg)														
	HMX	RDX	TNT	2,4 DNT	2,6 DNT	1,3,5 TNB	1,3,-DNB	2- ADNT	4-ADNT	2-NT	4-NT	3-NT	NB	Tetryl	NG
Crater Bottom	0.04	0.04	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	0.04
Crater Bottom (FD)	0.07	0.27	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	<0.02
Crater Walls	0.05	0.22	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	<0.02
Crater Wall (FD)	0.05	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	<0.02
Crater Rim South	0.12	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	<0.02
Crater Rim North	0.09	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	<0.02
Crater Bottom Deep (7.5-12cm)	0.10	0.30	1.30	<0.02	<0.02	<0.02	<0.02	0.12	0.05	NA	NA	NA	NA	<0.02	<0.02
Crater Bottom Deep (20-25cm)	0.09	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	NA	NA	NA	NA	<0.02	0.24
Water Samples from South Stream	Concentration of Explosives in Stream Water (ppb)														
	HMX	RDX	TNT	2,4 DNT	2,6 DNT	1,3,5 TNB	1,3,-DNB	2- ADNT	4-ADNT	2-NT	4-NT	3-NT	NB	Tetryl	NG
#1	0.06	0.69	<0.02	NA	NA	NA	NA	0.19	0.92	NA	NA	NA	NA	NA	NA
#2	0.05	0.60	0.04	NA	NA	NA	NA	0.22	0.22	NA	NA	NA	NA	NA	NA
#3	0.05	0.57	0.08	NA	NA	NA	NA	0.21	0.20	NA	NA	NA	NA	NA	NA

FD = Field duplicate.

relative to the soil concentrations suggested that this plant was actively taking up these residuals. Although the one plant sample showed a similar trend for HMX, the data set was too limited to support this as a conclusion.

Eupatorium compositifolium was not found at Site 3. RDX was detected in the tissue of *Yucca flaccida*, and on the surface of a plant identified as “lawn grass.” 1,3,5-TNB was detected in all Site 1 plant-tissue samples and the majority of samples from Sites 2 and 3. Di- and tetranitrotoluene were observed at levels ranging from 0.65 to 7.41 mg/kg in plant tissues from Sites 1 and 2.

Although there was no direct correlation determined between the vegetation and that concentration of residual in the surface soil, plants at both Site 1 and 2 showed a significant amount of energetic material on the surface as well as inside the tissue. Plant surface material may have existed as debris or dust deposited on the above-ground portion of the plant. When rinsed off of the plant and extracted, RDX was found to be the predominant explosive residual on the outside of the plant tissue. Dinitrobenzene and dinitrotoluenes were also found on the plant surfaces.

4.3 Prescribed Burn

An area of approximately 4 acres on C52-N was selected for the controlled burn based on the results from the initial site characterization. This area was predominantly an air-to-ground combat training area and the majority of bombing operations occurred in an area referred to as the “Cat’s Eye”, which encompassed the majority of the burn area. The area had a history of high-level activity for the Air Force and other branches of the military and presented the greatest opportunity for surface energetic contamination. The initial site characterization described in Section 4.2 showed this to be the case. The site sloped approximately 6.5 m from the north to the south. Evidence of surface-flow channels indicated a significant potential for runoff. Vegetation density varied considerably with a markedly lower density in the high-impact areas and increasing cover towards the southern boundary.

Burn monitoring included pre- and post-burn surface soil sampling, above and below ground temperature monitoring, dishes, pans, and migration column setups using a Test Soil of known TNT and RDX concentrations, and melting column setups with neat TNT and RDX. The grid sampling procedure described for the initial site characterization was used to sample the surface soils. Thermocouple stations were positioned in the center of the grids and the various test systems were placed around the thermocouple stations. Figure 4-15 is a set of photographs of the test systems taken following the burn. Note that the heat generated during the burn was sufficient to partially melt the thermocouple tripod’s aluminum leg (melting point of Al = 660°C). Following the burn, surface traps were setup to capture sediment and water in runoff during subsequent rainfall events. The following sections discuss the results from each of the monitoring systems.

4.3.1 Burn Observations and Weather Conditions. The fire was ignited at approximately 1,700 on August 6, 2004 and for safety reasons the project team was required to evacuate the site for the ignition. This prevented direct observation of the fire; however staff were permitted to view the burn from the range control tower approximately two miles away. From this observation point it appeared that the majority of the smoke generated from the fire subsided after approximately 4 hours. Most of the smoke was seen in the first 2 hours of the burn.

Jackson Guard personnel monitored the burn into the evening hours and reported that the last fire seen was at approximately 2,100. The 24-hour safety period was implemented at this time and no project personnel were permitted to enter the range until Sunday, August 8th, at 0830.

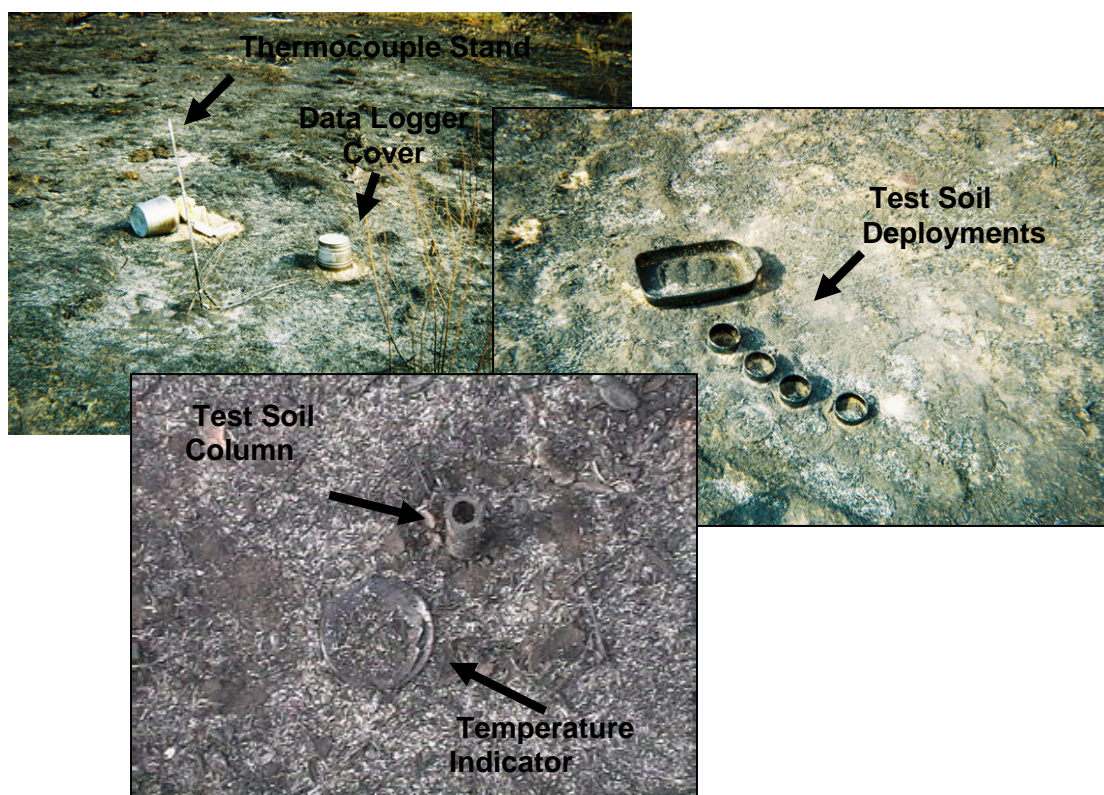


Figure 4-15. Post-Burn Photos of Test Systems

At the time of ignition the temperature was approximately 32°C with a humidity of approximately 33%. The wind was out of the east to northeast at about 10 mph. By 2100 when the burn appeared complete the temperature was approximately 28°C and the humidity was 45%. The wind at this time was out of the northeast at 7 mph. Generally these burn conditions were as good as possible in this region and season. Figure 4-16 illustrates the weather conditions on the day of the burn.

August in Northern Florida is typically subtropical, hot and humid. Weather was not recorded at the burn site, the weather conditions described here are from records at the Ft Walton Beach Airport (VPS) located approximately 15 miles southwest of the site. In July prior to the burn, 4.84 inches of rain fell as compared to the monthly average of 4.96 inches. In the August week predating the burn 1.06 inches of rain fell on August 1st but no precipitation was recorded again until 0.09 inches fell on August 9th. On August 10th heavy rains associated with tropical storm Bonnie resulted in approximately 6 inches of rainfall.

The coincidence of a dry period for several days before and after the burn was quite fortuitous allowing dry conditions leading up to and for the burn as well as for the sampling period after. The heavy rains that followed allowed for surface water samples to be collected from the newly burned area. This is discussed further in Section 4.3.7.

Observations of the burn impact were made once permission was given to re-enter the site at 0830 on August 8th. In general, the fire moved through the 4 acre area fairly quickly having a residence time of approximately 15-20 minutes in the measured areas and thoroughly burned all of the vegetation and pine straw on the surface of the test site area. The burn appeared complete within the test area and no

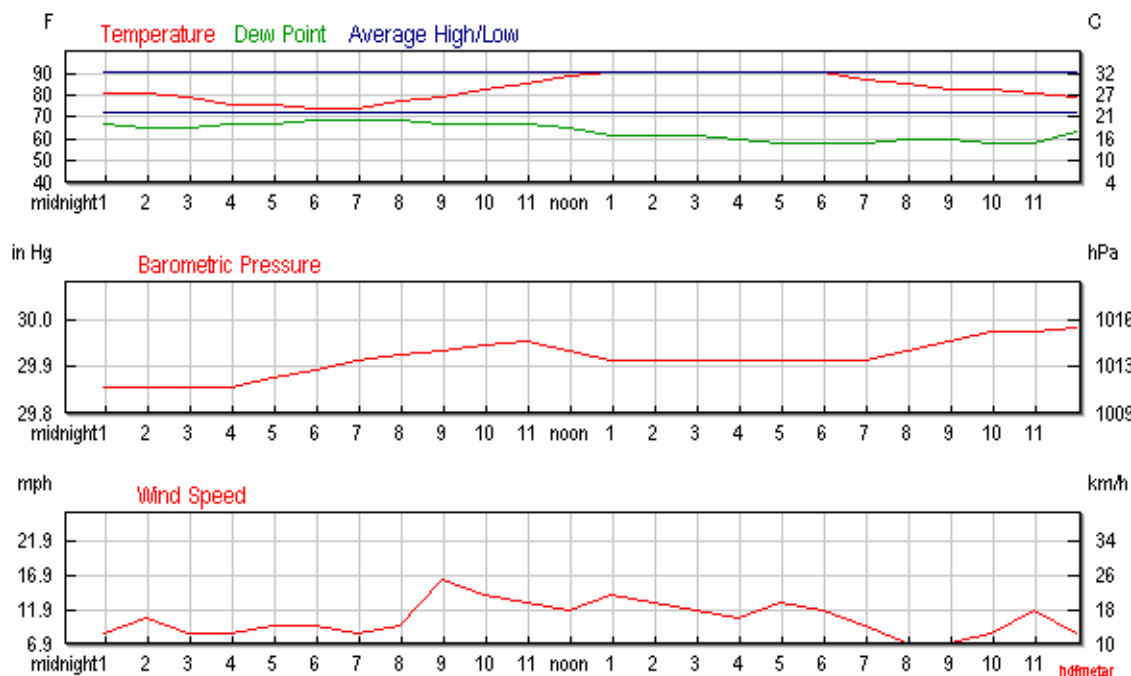


Figure 4-16. Weather Conditions During the Burn

unburned fuel was observed after the fire. Ash was all that was observed in the four acre burn area. The fire had gotten hot enough to melt and burn the rubber tires off of equipment that was used for targets and some of the aluminum tripods supporting the thermocouple stations had melted due to the fire, indicating that fire in some locations had reached temperatures of at least 660°C for some period of time. The fire did not carry into the non-burn control area located approximately 30 m to the north of the burn area. Mild east to northeasterly winds moved the fire to the south/southwest and advanced the burn down the hill where it died out due to lack of fuel at approximately 30 m south of test area E-3.

4.3.2 Temperature. Temperature readings were recorded every second following fire ignition from the six thermocouples at each of the four test locations. Figure 4-16 shows the temperature profiles for each thermocouple placement at each test area.

In general, the profiles showed a rapid rise in temperature above the ground surface, and hence above the placed fuel, followed by a fairly rapid decrease following the progression of the flame front. The decrease showed a slight tailing off as the temperatures returned to ambient levels. At the ground level, the profiles were characterized with a rapid rise in temperature followed by a gradual decrease and trailing off than observed for above the ground surface. At 2.5 cm bgs, the impact from the surface burn was less pronounced and showed a slight lag from the responses observed at or above the ground. The data from 7.6 cm bgs showed no temperature impact from the burn. As expected, there was no effect on the temperatures at the control site.

The maximum temperatures achieved at each thermocouple location are plotted as a function of fuel loading in Figure 4-17. During the burn the maximum temperature recorded at the control area (which was outside the influence of the fire) was 42°C and occurred at the ground surface. In the burn areas the data showed that the aboveground maximum temperatures recorded during the burn were a function of the fuel loading and that the temperature was consistently higher at the 30.5-cm height compared to the

91-cm height. The maximum temperature at 30.5 cm above the ground was 633.5°C and at the 91 cm height was 293.5°C. The maximum temperature at ground surface peaked at 511°C with the medium fuel loading and was lower (449°C) with the higher fuel loading. A heating effect was observed at the 2.5-cm depth with the maximum temperature of 96°C achieved at the medium fuel loading. At the low- and high-fuel loadings the maximum temperatures recorded at the 2.5 cm depth were 61.5°C and 56.5°C, respectively. There was no observable temperature effect at the 7.6-cm depth.

For the most part the temperature profiles were as expected. Previous fire ecology research has shown that the heat from near ground fires dissipates quickly, which is a necessity for prescribed burning to avoid canopy scorching or killing of taller and mature trees (Wade and Lunsford, 1990; Smith et. al., 2005). This was observed in this investigation by the much lower temperatures recorded at 91-cm ags versus 31.5 cm ags. The small temperature increase at the 2-cm depth and the lack of an observable temperature rise at the 7.6-cm depth was not totally unexpected given the short duration of the burn. Previous fire research has shown that heat penetration into soil is not necessarily a direct function of the fire intensity and that only 8 to 10% of the heat generated during the burn is transmitted downward (Hungerford et. al., 1990). In fact, temperature effects are impacted by several factors including the fuel type and loading, duration and intensity of the fire, moisture content of the fuel, and soil moisture (Massman et. al., 2003). Because soils typically have poor heat conducting properties, the temperature effect is attenuated over short depths (Valettte et al., 1994; Brooks, 2002; Massman et. al., 2003; Hubbard et al., 2004).

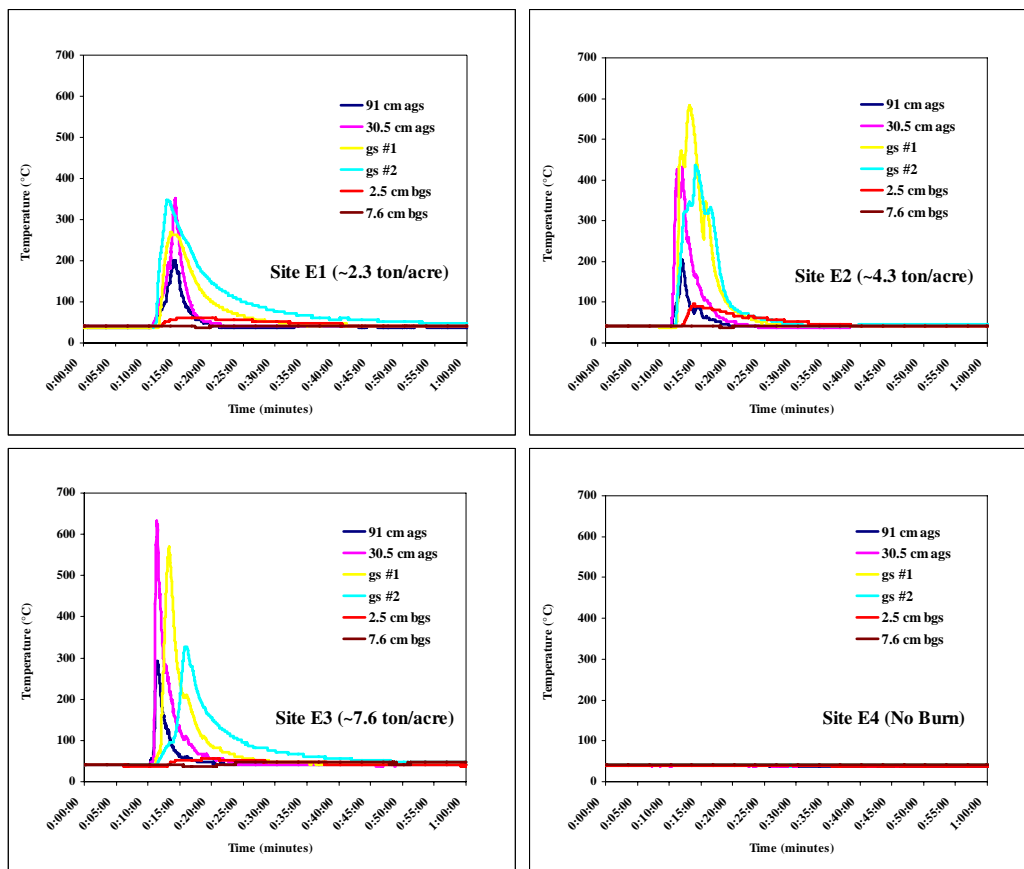


Figure 4-17. Temperature Profiles for Each Test Site During the Burn

In contrast to the direct correlation between increasing fuel loading and the higher temperatures recorded above the ground, the maximum-temperature profile at the ground surface and at the 2.5-cm depth indicated that there was a fuel loading (below the high-fuel loading) where soil heating was maximized. The reason for the decreased heating at the higher fuel loading could be attributed to the insulating of the ground from the thicker fuel layer, or to depleted oxygen, causing the fuel to smolder at lower temperatures as the burn progressed through the fuel layer.

The temperature data from the two ground-surface thermocouples at each test plot were averaged and graphed in Figure 4-18. Also imposed on the graph are two lines that correspond to 175°C and 250°C. These temperatures were shown in the laboratory experiments to promote rapid decomposition of RDX and TNT, respectively. At 175°C, the half life of 1,000 mg/kg of RDX was determined to be 5 minutes. The half life for 1,000 mg/kg of TNT at 250°C was determined to be less than 4 minutes.

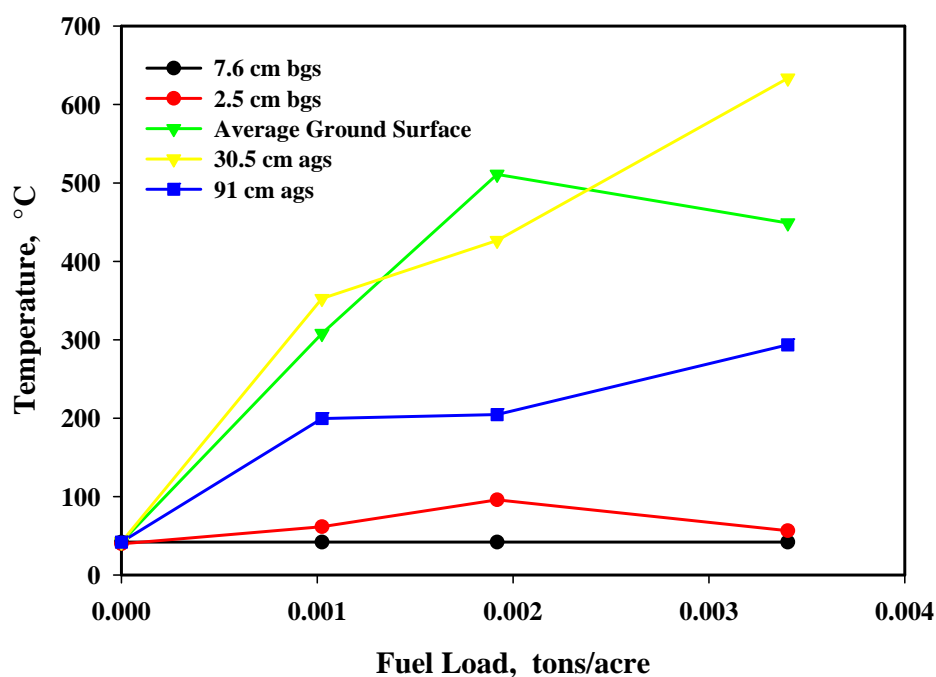


Figure 4-18. Maximum Temperatures Recorded as a Function of Fuel Loading

The intersections of the 175°C line with the temperature lines at all three fuel loadings shows that temperature was maintained for approximately 5.3, 6.5, and 5.3 minutes for the low, medium, and high fuel loadings, respectively (see Figure 4-16). This meant that the temperatures were high enough and sustained long enough to promote decomposition of at least 50% of RDX present at concentrations at or below 1,000 mg/kg. This is a conservative estimate for the potential RDX decomposition at the Eglin site for several reasons. First, the maximum temperatures achieved under all three fuel loads were significantly higher than 175°C, and therefore the half lives of RDX at temperatures above 175°C would be significantly less than the 5 minutes. Second, the 5 minute half life was determined in the laboratory for a concentration of 1,000 mg/kg and the highest soil concentration measured during the initial site characterization was two orders of magnitude less, which would also contribute to a shorter half life. Finally the field soils cooled more slowly than in the laboratory based experiments. This suggests that sufficiently high temperatures were achieved to expect substantial destruction of energetic materials on

the soil surface. The 250°C line for TNT shows that the time at which the temperature or greater was maintained was less than the time that 175°C was held for all three fuel loadings. The low, medium, and high fuel loadings maintained 250°C for 2.8, 5.6, and 3.5 minutes, respectively. Only the medium fuel load held 250°C for greater than 4 minutes. As with RDX, sufficiently high temperatures were achieved to destroy more than 50% of the TNT in the surface soil even though the critical temperature was not held under the low and high fuel loadings, the temperatures for all three fuel loadings were greater than 250°C, and the measured concentrations of TNT during the initial site characterization were also well below the 1,000 mg/kg concentration for which the 4-minute half life was calculated.

The potential for decomposition of TNT and RDX in the subsurface soils was not very high during the controlled burn. The temperatures at 2.5 cm bgs peaked at 61.5, 96.0, and 56.5°C for the low, medium, and high fuel loads, respectively. As can be seen in Figure 4-16, subsurface temperatures were held for longer periods than the higher temperatures at the ground surface, but they were significantly lower than the 175°C and 250°C critical temperatures. The fact that there was no heating of the soils at 7.6 cm bgs adds to the low potential for subsurface explosives residuals treatment during the controlled burn. The lack of heat transfer to any significant depth is similar to results from other fire ecology research using pine needles or other forest litter materials as the fuel sources (Agee, 1973; DeBano et. al., 1977; Bailey and Anderson, 1980; Frandsen and Ryan, 1986; Raison et. al., 1986; Hungerford et. al., 1991; Valette et. al., 1994; DeBano et. al., 1998; Neary et. al., 1999; Molina and Llinares, 2001; Brooks, 2002; Massman et. al., 2003; Boring et. al., 2004; Hubbard et. al., 2004). Although the needles burn at upwards of 600°C, the fires are short lived and the thicker pine needle beds can insulate the ground from the heat (Hartford and Frandsen, 1992). Research has shown that heavier fuels such as wood plant materials or logs, tend to heat the subsurface much more than pine straw (Bailey and Anderson, 1980; Hungerford et. al., 1991; Neary et. al., 1999). It might be possible to design a controlled burn that incorporates wood chips or bark mulch to increase the transfer of heat into the deeper subsurface.

Temperature indicator strips and disks were placed on the ground at various locations around each test plot, and on the bottom of the dishes and pans that were filled with test soil. All indicators placed on the ground in the test areas that were burned were maximized out (i.e., greater than 260°C), which correlated with the temperatures indicated by the thermocouples. The indicators at the bottom of the dishes reacted within their temperature ranges and the averages from the three dishes are provided in Table 4-13. The data showed that the temperatures were a function of soil depth and interestingly an inverse function of fuel loading. In general, the temperature readings were in good agreement with the thermocouple readings from the 2.5-cm depth for the low fuel (E1) and high fuel (E3) test areas but significantly lower for the medium fuel (E2) test area that demonstrated the highest temperature at that depth outside the dishes.

Table 4-13. Averaged Temperatures Recorded from Indicators on the Bottom of the Dishes Filled with Test Soil at Varied Thickness

Thickness of Soil in Dish	Average Temperatures at the Bottom of Dish (°C) ^(a)			
	Test Area E-1	Test Area E-2	Test Area E-3	Test Area E-4
1 cm (Test Soil)	80	77	67	51
2 cm (Test Soil)	69	62	60	46
3 cm (Test Soil)	60	58	54	45
2 cm (control soil – clean sand)	76	54	56	43

(a) Average of triplicate dishes placed at north, west, and south boundaries of the central circle (see Figure 3-5).

E-1 = low fuel; E-2 = medium fuel; E-3 = high fuel

The discrepancy between the fuel loading and temperature impacts observed with the thermocouples versus the indicator disks/strips could be due to differences in soil moisture between the Test Soil and the site surface soil, a difference in heat conduction properties between the soil, or an artifact of having the Test Soil in dishes with closed bottoms and a side wall. A soil-moisture effect would mean that the moisture in the Test Soil should have been higher than the moisture content of the site surface soil given the results observed from the lab experiments. This was ruled out as there was rain a few days before the burn, and the fact that the Test Soil went through a series of preparation stages where significant drying occurred. It was possible that the two soils had different heat conductance properties, however both soils were sandy and a difference in heat conductance should have affected the temperatures consistently across the soil loadings in such a way that the temperature profile would reflect the higher temperature at the medium fuel load. The most likely scenario is that having the soils in the dishes affected the temperature. The decreasing temperature trend across the increasing fuel loads at all soil depths suggested that the burn at the soil-fuel interface within the dishes may have become oxygen limited, which in turn caused a decrease in the temperature of the burn. This is corroborated by the observed lack of residual explosives decomposition in these dishes (see Section 4.3.3). Unfortunately, there were no indicators or thermocouples on the soil surface within the dishes.

4.3.3 Explosive Residual Concentrations in Pre- and Post-Burn Surface Soils. The analyses of the surface soils collected from all four locations were very low and even below detection for the majority of the samples making it impossible to assess the effect of the burn on those samples. The concentrations measured during the initial site characterization indicated sufficient contamination for locating the four test plots. Even though 15 months had passed between the initial site characterization and the controlled burn, the lack of sufficient contamination at the time of the burn was somewhat unexpected. One of the main reasons for the extended time between the two events was the heavy use of the range by the Air Force and other DoD branches and it was thought that those activities would have deposited additional explosives residues. However, one or any combination of reasons could explain the disappearance of the contamination over the time period between the initial site characterization and the conductance of the burn. The results for the surface soil samples collected prior to- and following the burn are shown in Tables 4-14 through 4-17. One explanation for the reduced explosives concentrations is that percolation of rainfall facilitated transport of the surface and near-surface explosive residuals deeper into the subsurface. The sandy soils at Eglin would be expected to easily leach TNT, RDX, and HMX. While the potential for percolation facilitated advective migration exists, data from the surface traps suggests that the soils have a capacity for binding explosive residuals. As such, it is doubtful that percolation could explain all of the observed decrease.

Another possible mechanism for reducing the explosives concentrations is plant uptake. The data previously discussed in Section 4.2.2 showed that the plants at Eglin actively uptake TNT and RDX as well as other residual compounds. The vegetation at the site was noticeably greener and denser at the time of the burn (see Figure 4-19). Two growing seasons occurred between the initial site characterization and the burn and it is possible during those cycles the explosives in the soil were taken up into the plant tissue, degraded within the plants, and/or biodegraded in the root zone. The potential for phytoremediation of explosive compounds has been demonstrated in the literature as mentioned previously (Section 1.0).

It is also possible that the area burned during the 15 month period before the test. While no records of such a burn exist small localized fires are commonly ignited by detonations and if they are brief and self limiting no record would exist. There was no clear evidence of such a burn, but qualitative observation indicated that fuel levels were less at the time of the burn than they had been at the time of the characterization sampling.

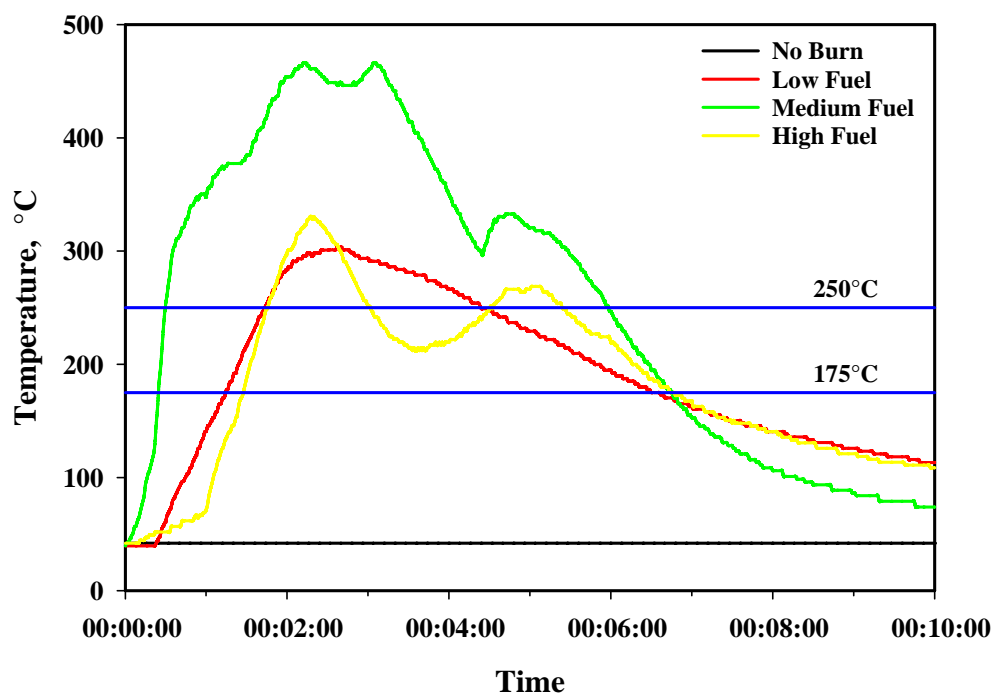


Figure 4-19. Averaged Temperature Profiles from the Two Ground-Surface Thermocouples at Each of the Four Test Plots

Even though it was not possible to assess the effectiveness of the burn for reducing soil-phase explosive residuals concentrations, the temperature data generated during the burn showed that the temperatures achieved were sufficiently high to support thermal decomposition of TNT and RDX. At the concentrations measured in during the initial site characterization and at the temperatures recorded during the burn it would be expected that TNT, RDX and other energetics on the soil surface and on or within the plants would have been destroyed during controlled burning.

4.3.4 Explosive Residual Concentrations in Test Soil in Dishes and Pans. The pre- and post-burn TNT and RDX concentrations in soil placed in the Pyrex™ dishes were averaged and the results are plotted in Figures 4-20 and 4-21, respectively. Post-Burn Energetic concentrations in test soils for all test areas including the non-burn control were similar and the statistical significance of the data was masked by the variability among replicates. Overall, TNT removal at the lowest fuel loading in the 1-cm soil thickness dishes and in the highest fuel loading for the 2-cm thickness were the only conditions where the post-burn concentrations were statistically lower than the control dishes, however, those average concentrations were not significantly different than the average concentrations from the other dishes in the burn areas with the same soil depths.

For RDX, only the low fuel condition for the 1-cm thickness soil dishes showed average post-burn soil concentrations that were significantly lower than the respective control. The general trend for that setup showed greater RDX decreases with lower fuel loadings. The 2-cm dishes showed a significantly lower RDX concentration in the post-burn soil at the highest fuel loading compared to the control dish and the low fuel condition, but not compared to the medium fuel loading. The 3-cm dishes all showed lower averaged post-burn RDX concentrations compared to the control dishes but none of the differences were statistically significant.

Table 4-14. Results from Surface Soil Samples Prior To- and Following the Controlled Burn at E-1

Composite Sample ID	Pre-Burn Energetic Concentrations (ppm)				Post-Burn Energetic Concentrations (ppm)			
	HMX	RDX	2,4,6 TNT	2,4 DNT/2,6 DNT	HMX	RDX	2,4,6 TNT	2,4 DNT/2,6 DNT
E1-A1	< 0.25	< 0.25	< 0.25	< 0.25	17.56	157.74	< 0.25	< 0.25
E1-A2	< 0.25	< 0.25	< 0.25	< 0.25	1.41	< 0.25	9.79	< 0.25
E1-B1	1.22	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E1-B2	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E1-B3	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E1-B3 (FD)	< 0.25	< 0.25	< 0.25	< 0.25	NA	NA	NA	NA
E1-B4	< 0.25	< 0.25	< 0.25	< 0.25	1.85	2.04	< 0.25	< 0.25
E1-C1	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E1-C2	< 0.25	2.66	< 0.25	< 0.25	< 0.25	< 0.25	4.36	< 0.25
E1-C3	< 0.25	< 0.25	1.61	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E1-C3 (AD)	< 0.25	< 0.25	1.36	< 0.26	NA	NA	NA	NA
E1-C4	< 0.25	< 0.25	< 0.25	< 0.25	1.04	7.15	< 0.25	< 0.25
E1-C4 (AD)	NA	NA	NA	NA	1.17	7.51	< 0.25	< 0.25
E1-C5	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E1-C6	1.66	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E1-C7	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E1-C7 (AD)	NA	NA	NA	NA	< 0.25	< 0.25	< 0.25	< 0.25
E1-C8	< 0.25	< 0.25	< 0.25	< 0.25	1.75	11.90	< 0.25	< 0.25

AD = Analytical duplicate

FD = Field duplicate

NA = Not applicable

Lower detection limit = 0.25 ppm

Table 4-15. Results from Surface Soil Samples Prior To- and Following the Controlled Burn at E-2

Composite Sample ID	Pre-Burn Energetic Concentrations (ppm)				Post-Burn Energetic Concentrations (ppm)			
	HMX	RDX	2,4,6 TNT	2,4 DNT/2,6 DNT	HMX	RDX	2,4,6 TNT	2,4 DNT/2,6 DNT
E2-A1	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E2-A2	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E2-A2 (FD)	< 0.25	< 0.25	< 0.25	< 0.25	NA	NA	NA	NA
E2-B1	5.78	< 0.25	< 0.25	< 0.25	< 0.25	3.06	< 0.25	< 0.25
E2-B2	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E2-B2 (AD)	< 0.25	< 0.25	< 0.25	< 0.25	NA	NA	NA	NA
E2-B3	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E2-B3 (AD)	NA	NA	NA	NA	< 0.25	< 0.25	< 0.25	< 0.25
E2-B4	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E2-C1	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E2-C2	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E2-C3	< 0.25	2.33	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E2-C4	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E2-C5	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E2-C6	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E2-C7	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E2-C8	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E2-C8 (AD)	< 0.25	< 0.25	< 0.25	< 0.25	NA	NA	NA	NA
E2-C8 (FD)	NA	NA	NA	NA	< 0.25	< 0.25	< 0.25	< 0.25
E2-C8 (AD of FD)	NA	NA	NA	NA	< 0.25	< 0.25	< 0.25	< 0.25

AD = Analytical duplicate

FD = Field duplicate

NA = Not applicable

Lower detection limit = 0.25 ppm

Table 4-16. Results from Surface Soil Samples Prior To- and Following the Controlled Burn at E-3

Composite Sample ID	Pre-Burn Energetic Concentrations (ppm)				Post-Burn Energetic Concentrations (ppm)			
	HMX	RDX	2,4,6 TNT	2,4 DNT/2,6 DNT	HMX	RDX	2,4,6 TNT	2,4 DNT/2,6 DNT
E3-A1	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	6.90	< 0.25	< 0.25
E3-A2	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	6.45	< 0.25
E3-B1	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	2.41	< 0.25	< 0.25
E3-B2	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E3-B3	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E3-B4	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E3-C1	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	0.84	< 0.25
E3-C2	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E3-C3	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	25.32	< 0.25
E3-C4	< 0.25	< 0.25	< 0.25	< 0.25	0.96	9.40	0.79	< 0.25
E3-C4 (FD)	< 0.25	< 0.25	< 0.25	< 0.25	NA	NA	NA	NA
E3-C4 (AD)	< 0.25	< 0.25	< 0.25	< 0.25	NA	NA	NA	NA
E3-C4 (AD)	NA	NA	NA	NA	0.97	9.43	0.67	< 0.25
E3-C4 (FD)	NA	NA	NA	NA	< 0.25	< 0.25	< 0.25	< 0.25
E3-C5	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E3-C6	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E3-C7	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E3-C8	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25

AD = Analytical duplicate

FD = Field duplicate

NA = Not applicable

Lower detection limit = 0.25 ppm

Table 4-17. Results from Surface Soil Samples Prior To- and Following the Controlled Burn at E-4

Composite Sample ID	Pre-Burn Energetic Concentrations (ppm)				Post-Burn Energetic Concentrations (ppm)			
	HMX	RDX	2,4,6 TNT	2,4 DNT/2,6 DNT	HMX	RDX	2,4,6 TNT	2,4 DNT/2,6 DNT
E4-A1	< 0.25	< 0.25	< 0.25	< 0.25	2.69	< 0.25	< 0.25	< 0.25
E4-A2	< 0.25	2.49	< 0.25	< 0.25	< 0.25	< 0.25	1.61	
E4-B1	< 0.25	1.51	< 0.25	< 0.25	< 0.25	2.80	< 0.25	< 0.25
E4-B2	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E4-B3	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E4-B3 (AD)	< 0.25	< 0.25	< 0.25	< 0.25	NA	NA	NA	NA
E4-B3 (AD)	NA	NA	NA	NA	< 0.25	< 0.25	< 0.25	< 0.25
E4-B4	2.77	1.24	< 0.25	< 0.25	2.97	< 0.25	< 0.25	< 0.25
E4-C1	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E4-C1 (FD)	NA	NA	NA	NA	< 0.25	< 0.25	< 0.25	< 0.25
E4-C2	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	4.36
E4-C2 (FD)	< 0.25	1.22	< 0.25	< 0.25	NA	NA	NA	NA
E4-C3	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	0.95	< 0.25	2.20
E4-C4	< 0.25	< 0.25	< 0.25	< 0.25	1.20	< 0.25	< 0.25	< 0.25
E4-C5	1.55	2.16	< 0.25	< 0.25	2.26	< 0.25	< 0.25	< 0.25
E4-C6	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E4-C7	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	1.15	< 0.25	< 0.25
E4-C8	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25	< 0.25
E4-C8 (AD)	< 0.25	< 0.25	< 0.25	< 0.25	NA	NA	NA	NA
E4-C8 (AD)	NA	NA	NA	NA	< 0.25	< 0.25	< 0.25	< 0.25

AD = Analytical duplicate

FD = Field duplicate

NA = Not applicable

Lower detection limit = 0.25 ppm

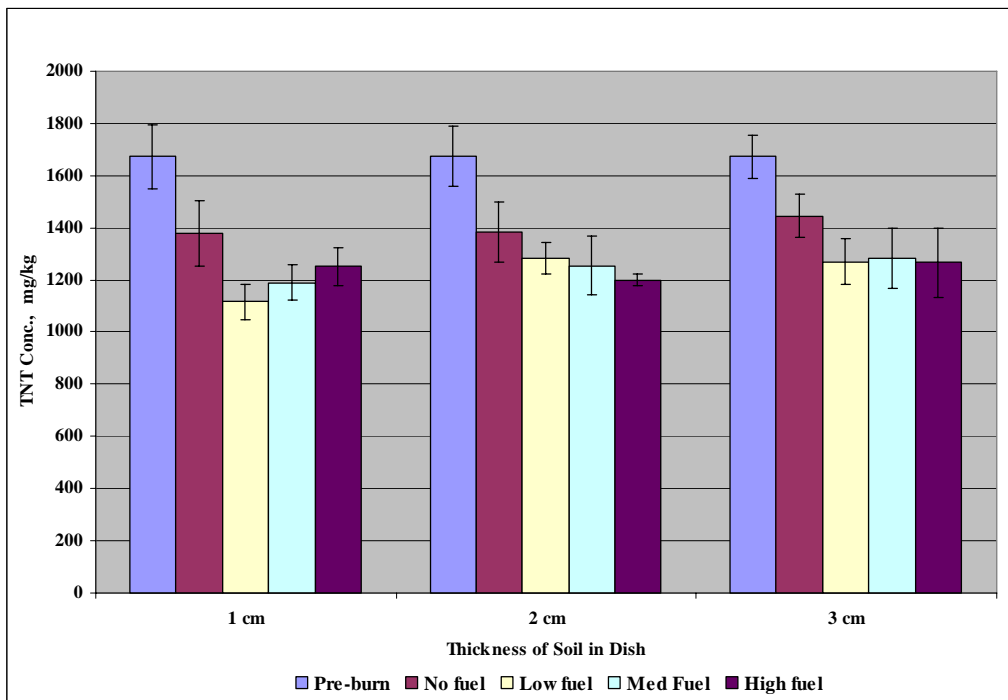


Figure 4-20. TNT Concentrations in Soil Dishes After the Burn as a Function of Fuel Load and Soil Layer Thickness

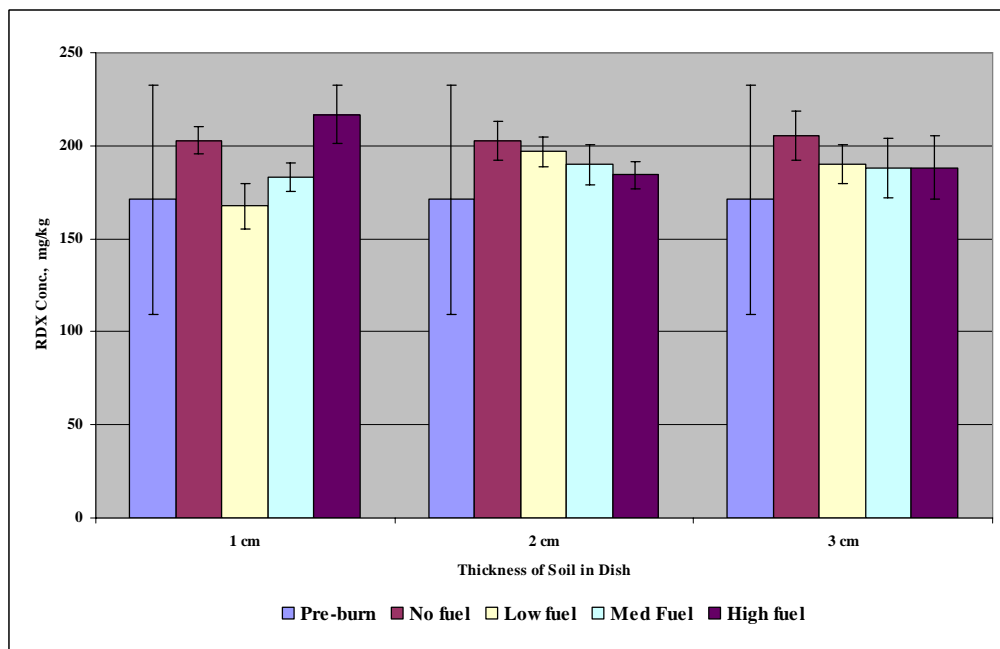


Figure 4-21. RDX Concentrations in Soil Dishes After the Burn as a Function of Fuel Load and Soil Layer Thickness

The relatively low degree of TNT and RDX reductions was unexpected but could be explained due to factors that were learned over the course of the burn. The dishes themselves may have reduced heat transfer to the soils within them. The dishes had the pine straw placed over their tops. During the burn, it is possible that the atmospheres in the dishes became oxygen deficient. The trend of increased removal with lower fuel loadings observed in the 1-cm soil thickness dishes supports this possibility and also suggests that there may have been an insulating effect from the thicker blanket of pine needles. This insulating effect is further supported by the apparent lag in temperature increase at the ground surface observed with increasing fuel load (see Figure 4-16). The depleted oxygen would have caused the temperature of the burning pine straw to be lowered, and would have decreased the potential for explosives thermal decomposition. The combination of the two caused the level of treatment to be masked within the variability of the explosive residuals concentrations.

To further illustrate the potential effect that oxygen limitation had on the thermal decomposition of TNT and RDX, the averaged concentration reductions were calculated and plotted in Figure 4-22. The trend of decreasing removal with increasing fuel load would be unexpected if not for the depleted oxygen level preventing the effective decomposition of the TNT and RDX. Under available oxygen conditions, it would be expected that the amount of concentration decrease would increase with fuel loading until the maximum level of treatment was achieved. The oxygen limitation phenomenon is further supported by the laboratory results discussed in Sections 4.1.1 and 4.1.2.

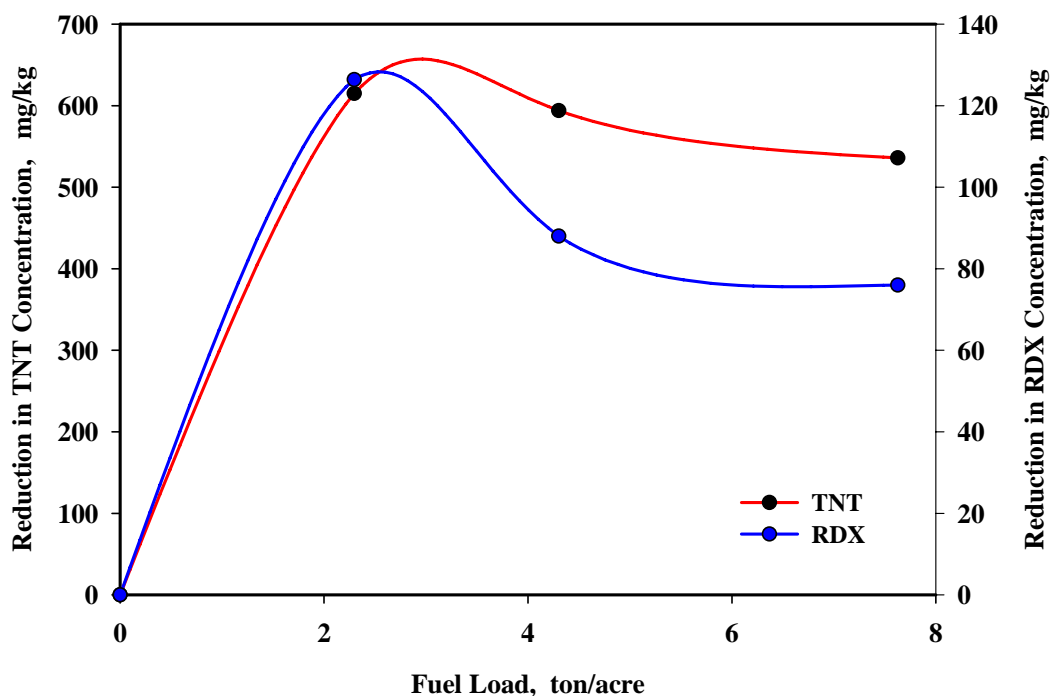


Figure 4-22. TNT and RDX Concentration Reductions as a Function of Fuel Load

Placing the pans with 5 cm of Test Soil was not included in the original experimental design but included as a means to provide more post-burn soil in the event that additional analyses were needed. Although such analyses were not deemed necessary, the soil from the pans was analyzed for TNT and RDX

concentrations and the results from the three pans at each test plot were averaged and are listed in Table 4-14. TNT destruction was approximately 55 % at low fuel loading, 54% at moderate, and 50 % at the heaviest fuel loading. RDX destruction was approximately 60 % at low fuel loading, 37% at moderate, and 30 % at heaviest fuel loading. Although the scatter in the data within each test plot masked the statistical significance, the trend was similar to that observed with the 1-cm soil dishes.

Table 4-18. Averaged Residual TNT and RDX Concentrations in Test Soil Placed in Pans

Test Area	Fuel Load (tons/acre)	TNT Concentration (ppm)		RDX Concentration (ppm)	
		Pre-Burn	Post-Burn	Pre-Burn	Post-Burn
E1	2.3	1673 ± 107	749 ± 295	171 ± 62	69.0 ± 38
E2	4.3		770 ± 250		107 ± 54
E3	7.6		828 ± 411		119 ± 81
E4	NA		1,364 ± 120		195 ± 13

NA = Not applicable – no fuel was added and this area served as the non-burn control area.

4.3.5 Migration Columns. The Test Soil migration columns were recovered after the fire and shipped to Battelle’s Labs in Columbus, OH for leach testing and soil explosives residual profiling. Table 4-19 shows the results from the migration column testing. The test soil layer was approximately 1.25 cm thickness with a diameter of 2.5 cm. Based on the initial Test Soil concentrations of 1,673 mg-TNT/kg-soil and 171 mg-RDX/kg-soil, the initial masses of each compound in the columns ranged between approximately 8.2 to 9.2 mg for TNT and approximately 0.84 to 0.90 mg for RDX.

Table 4-19. Explosives Residual Distribution (mg) and Mass Removal from Migration Column Experiments

Column Segment/Leachate	Average Energetic Mass as a Function of Depth in Triplicate Columns per Test Area and Field Blank (mg)									
	Low Fuel (2.3 ton/acre)		Moderate Fuel (4.3 ton/acre)		High Fuel (7.6 ton/acre)		Unburned Control		Field Blank	
	TNT	RDX	TNT	RDX	TNT	RDX	TNT	RDX	TNT	RDX
0 – 2.5 cm (initial mass)	8.64	0.89	8.77	0.90	8.17	0.84	9.17	0.94	8.68	0.89
0 – 2.5 cm (post burn)	0.05	ND	0.07	ND	0.05	ND	6.17	0.86	10.3	0.6
2.5 – 8.9 cm (post burn)	ND	ND	ND	ND	ND	ND	0.12	0.02	0.22	ND
8.9 – 15.2 cm (post burn)	ND	ND	ND	ND	ND	ND	0.11	0.02	0.13	ND
15.2 – 21.6 cm (post burn)	ND	ND	ND	ND	ND	ND	0.11	0.01	0.17	ND
21.6 – 28 cm (post burn)	ND	ND	ND	ND	ND	ND	0.11	0.02	0.18	0.01
Leachate (post burn)	0.02	ND	0.05	ND	0.02	ND	0.13	0.02	0.37	0.05
Percent Mass Removed – Assumed Destroyed	99	100	98.6	100	99	100	26.5	0.3	0 ^(a)	25

(a) over-recovered TNT in the field blank

ND = not detected

Approximately 15 mL of water were passed through the soil at 5-mL per hour while collecting the leachate from the bottom of the columns. Once gravity draining was completed, the soils were removed from the columns and segmented into discrete depth intervals. The soils were extracted and the extracts and the leachates were analyzed for explosives concentrations. Mass balance calculations of the columns showed significant reductions in both TNT and RDX due to the burn with nearly 99% of the TNT and

100% of the RDX removed. Approximately 73% of TNT and 99% of the RDX were recovered from the non-burn control. Greater than 100% of the TNT and 75% of the RDX were recovered from the field blank sample, which was taken to the field but not installed, and then brought back to the lab for leaching and analyses. Comparing the data from the columns that were placed in the burned plots against the data from the non-burn control and the field blanks indicated no apparent enhancement of mobility in the columns exposed to the fire.

The TNT and RDX removal from the columns was consistent across all of the burn conditions and were higher than observed for the dishes and/or pans. This was determined to be a more realistic representation of what would occur in the top soil layer under normal fire conditions for two reasons. First, the depths of the soil in the columns was much greater (24 times) the depth of the Test Soil, which acted as a source of oxygen to support the thermal decomposition as the fire passed over the lip of the column. During prescribed burning, soil oxygen is consumed at the soil/fuel interface. The second potential factor for the enhanced removals was the soil moisture from the soil column could facilitate stripping of the TNT and RDX as the water is boiled off and forms steam that then moves up through the contaminated soil layer.

4.3.6 TNT/RDX Melting Columns. The averaged results from the TNT and RDX melting columns for each of the three test areas that were burned are shown in Table 4-20. Test columns could not be retrieved from the non-burn control nor trip blanks be shipped back to laboratory for analysis due to security and safety issues.

Table 4-20 also shows the averaged mass balance results for triplicate TNT and RDX melting columns located in test areas E-1, E-2, and E-3. At test area E-1, all of the TNT (originally in the surface layer) was recovered in the top half section of the column, indicating that it had migrated most probably due to melting. In the first 1.3 cm approximately 615 mg was recovered. In the 1.3 cm to 3.8 cm section approximately 397 mg had mobilized, and in the 3.8 to 6.35 cm layer, the remaining 10 mg was recovered. In the RDX columns from test area E1 all RDX was assumed to have been reduced.

Table 4-20. Explosives Residual Distribution (mg) and Mass Removal from Melting Column Experiments

Column Segment	Average Energetic Mass as a Function of Depth in Triplicate Columns per Test Area (mg)					
	Low Fuel (2.3 ton/acre)		Moderate Fuel (4.3 ton/acre)		High Fuel (7.6 ton/acre)	
	TNT	RDX	TNT	RDX	TNT	RDX
0 – 1.3 cm (initial mass)	1000	1000	1000	1000	1000	1000
0 – 1.3 cm (post burn)	615	ND	645	ND	57	ND
1.3 – 3.8 cm (post burn)	10	ND	185	ND	129	ND
3.8 – 6.3 cm (post burn)	397	ND	ND	ND	60	ND
6.3 – 28 cm (post burn)	ND	ND	ND	ND	4.3	ND
Percent Mass Removed – Assumed Destroyed	0	100	17	100	75	100

ND = not detected

In columns located in Test Area E-2 only 83% of the TNT was recovered, with 645 mg mobilized to 1.3 cm and 185 recovered in the 1.3 to 3.8 cm layer. All RDX was assumed to have been removed at E-2. In columns located in test area E-3 only 25 % of the TNT was recovered, with the remainder assumed to have been removed. RDX is assumed to have been completely removed from the columns at E-3.

4.3.7 Energetic Residuals in Surface Water Runoff and Trapped Sediment. The on-range surface water runoff traps were sampled after two significant storm events in the region, tropical storm Bonnie and Hurricane Charlie. Although there were no detectable energetic residuals found in the soluble phase, several traps resulted in low mg/kg detections of energetics in the migrated sediments indicating that surface sediment transfer through rain events may be a significant transport mechanism at this site. Figure 4-23 shows the rain fall in the area during these two significant storm events and shows the approximate time that field staff obtained access to the range to sample the traps.

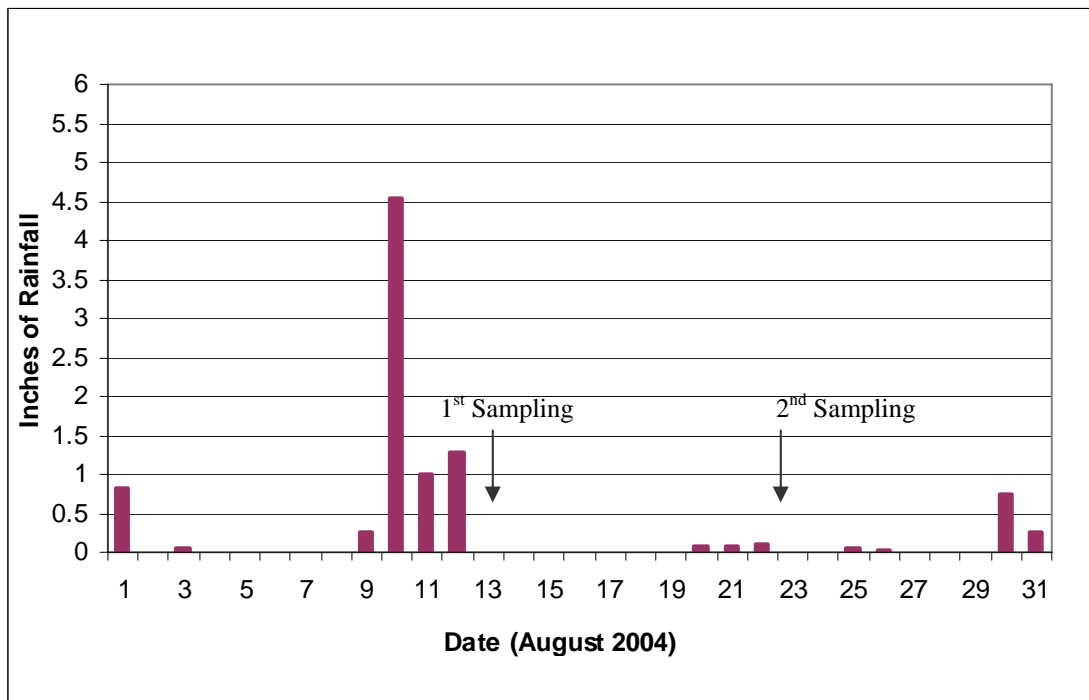


Figure 4-23. Significant Rainfall Events Relative to Surface Water Trap Sampling Activities

Table 4-21 shows the results obtained from the two sampling events. The higher occurrence of transfer occurred after the first event in August 13, 2004 with less detected in traps on August 23, 2004.

Table 4-21. Results from Surface Water Run Off Traps after Two Sampling Events

Sampling Event	Trap ID	Surface Water (mg/L)		Sediment (mg/kg)	
		TNT	RDX	TNT	RDX
#1 (August 13, 2004)	E-SW-1	< 0.25	< 0.25	26.82	< 0.25
	E-SW-2	< 0.25	< 0.25	5.18	< 0.25
	E-SW-3	< 0.25	< 0.25	1.95	3.63
	E-SW-4	< 0.25	< 0.25	< 0.25	< 0.25
	E-SW-5	< 0.25	< 0.25	1.25	6.08
	E-SW-6	< 0.25	< 0.25	2.37	< 0.25
	E-SW-7	< 0.25	< 0.25	2.94	1.94
	E-SW-8	< 0.25	< 0.25	1.17	6.32
	E-SW-9	< 0.25	< 0.25	< 0.25	< 0.25
	E-SW-10	< 0.25	< 0.25	2.27	< 0.25
	E-SW-11	< 0.25	< 0.25	< 0.25	< 0.25
	E-SW-12	< 0.25	< 0.25	< 0.25	< 0.25
	E-SW-13	< 0.25	< 0.25	< 0.25	< 0.25
	E-SW-14	< 0.25	< 0.25	< 0.25	< 0.25
	E-SW-15	< 0.25	< 0.25	< 0.25	< 0.25
Average		< 0.25	< 0.25	5.49	4.49
#2 (August 23, 2004)	E-SW-1	< 0.25	< 0.25	< 0.25	2.87
	E-SW-2	< 0.25	< 0.25	< 0.25	< 0.25
	E-SW-3	< 0.25	< 0.25	< 0.25	< 0.25
	E-SW-4	< 0.25	< 0.25	< 0.25	< 0.25
	E-SW-5	< 0.25	< 0.25	< 0.25	3.12
	E-SW-6	< 0.25	< 0.25	< 0.25	1.95
	E-SW-7	< 0.25	< 0.25	< 0.25	< 0.25
	E-SW-8	< 0.25	< 0.25	< 0.25	< 0.25
	E-SW-9	< 0.25	< 0.25	< 0.25	< 0.25
	E-SW-10	< 0.25	< 0.25	< 0.25	< 0.25
	E-SW-11	< 0.25	< 0.25	< 0.25	< 0.25
	E-SW-12	< 0.25	< 0.25	< 0.25	< 0.25
	E-SW-13	< 0.25	< 0.25	< 0.25	< 0.25
	E-SW-14	< 0.25	< 0.25	< 0.25	< 0.25
	E-SW-15	< 0.25	< 0.25	< 0.25	< 0.25
Average		< 0.25	< 0.25	< 0.25	2.65

LDL = 0.25 mg/kg

5.0 CONCLUSIONS

Based on this study it is clear that controlled burning can heat surficial soils to the point that thermal destruction of TNT and RDX will occur. This is supported by laboratory data demonstrating temperatures necessary for destruction, field measurements of temperature during the controlled burn and analysis of soils before and after the burn. It is also clear that TNT, RDX and other energetics were found in and on plant tissue prior to the burn and that these were destroyed in the burn. Numerous lessons were learned about the problems associated with monitoring an experiment of this kind; energetics are heterogeneously distributed in soils and their concentrations change over time, making before and after burn soil sampling results of limited value. Much of our test monitoring relied on soils placed in various containers immediately before and then analyzed immediately after the burn, this was in anticipation of the problem of soil heterogeneity, unfortunately many of these containers had bottoms and were discovered not to be representative; columns appeared to have worked better. Fuel was added to the site, as is common practice to insure burn across sparsely vegetated areas. It appears that at the use of too much fuel may actually insulate the ground surface and reduce soil temperatures and the destruction of energetics. In the end the experiments were successful and given the first time nature of this work, the problems encountered were not surprising. More detailed conclusions follow.

5.1 Conclusions Drawn from Laboratory Testing

1. The thermal decomposition of TNT and RDX is a function of temperature, concentration, soil moisture, and soil chemistry and other physical properties
2. Generally, higher temperatures and lower soil concentrations result in more rapid decomposition of TNT and RDX.
3. Oxygen is required to support thermal decomposition.
4. Soil-associated TNT and RDX decompose at temperatures consistent with those observed in the field (175°C – RDX and 250°C TNT).

5.2 Conclusions Drawn from the Field Demonstration

The following conclusions are based on the results and observations made during the controlled burn at C52N.

1. Certain plants can actively uptake explosive residuals and the compounds and plants at C-52N can be compound specific. At C52N, *Eupatorium compositifolium* showed increasing in-tissue concentrations against decreasing soil concentrations. Other plant species were analyzed with in-tissue TNT, RDX, and/or HMX but the correlation with soil concentrations was not apparent.
2. TNT and RDX concentrations in the soil at the test area are subject to change due to any one or combination of plant uptake, advective transport to the groundwater during infiltration of rainwater, or sediment transport during high intensity rainfall events. The three actively burned test areas were all located in areas that were previously characterized with low mg/kg concentrations of TNT and RDX. None of these locations showed such contamination in the pre-burn samples despite the continued use of the range.
3. During controlled burning, temperatures at ground surface and above can reach levels that support rapid thermal decomposition. Laboratory testing showed temperatures near

250°C resulted in rapid decomposition of both TNT and RDX. Field temperature measurements showed ground-surface temperatures near 600°C in several locations.

4. Heat generated during the controlled burn did not penetrate into the ground for more than a few centimeters. At test areas E2 and E3, where temperatures at ground surface reached near 600°C, the maximum temperatures achieved at 2.5 cm below grade were 96°C and 52.5°C, respectively. There was no temperature effect observed at 8.5 cm bgs at any of the test area locations.
5. Pine straw burns hot, is effective at carrying a burn, but is not effective at heating the subsurface soil. Previous research has shown that heat penetration into soil is a function of both the intensity and duration of the fire. The pine straw burned too rapidly heating the ground surface for less than 10 minutes in most cases, which was not of sufficient length to heat the soil. Temperature data suggested that thicker beds of needles acted as an insulator as the fire passed. The increased fuel loading appeared to lower the temperature of the burn on the underside of the needle bed.
6. Test systems (dishes or pans) that are enclosed on all sides and the bottom limit the supply of oxygen, which in turn affects the degree of thermal decomposition. These turned out not to provide representative data.
7. The open bottom column configuration was more representative of the impact that fire would have on TNT and RDX in soil under natural conditions than the dishes and pans.
8. Neat TNT can migrate downward into the soil profile if temperatures are not sufficiently high enough for it to rapidly decompose. Average recoveries of the original 1-gram of neat TNT over a 15 cm depth profile in the melting columns were 102%, 83%, and 25% for the low, medium, and high fuel loadings, respectively.
9. Neat RDX does not have the same propensity as TNT to melt and migrate into the soil. The melting point temperature for RDX is closer to its decomposition point, 204°C versus 260°C, respectively. There was no RDX recovered from the soil profile in any of the melting columns under any fuel loading.
10. The migration columns showed that under controlled burning conditions more than 98.5% of the TNT and 100% of the RDX was thermally decomposed from the 1-cm layer of Test Soil.
11. Surface water with entrained sediment is a transport mechanism for TNT and RDX at this site. Analyses of water and sediment from the surface traps showed explosives residuals associated with the sediment while concentrations in the water were below the detection limit of 025 mg/L.

The overall conclusion from the FERM investigation was that using prescribed burning on ranges has potential for destroying a significant amount of explosives residual in surface soils and in and on plant tissues. Incorporating a well-planned approach that takes into account specific considerations of each range could be an effective tool for minimizing the impacts of explosives residuals on groundwater and local surface water bodies. It is anticipated that FERM would be a component of a multi-component program for managing explosives residuals resulting from testing, training, and EOD operations on ranges. While the SERDP demonstration described in this report has accomplished the objective of providing preliminary evidence for the potential for using FERM for this intended purpose, additional work is needed to better understand plant uptake of explosive residuals, to quantify the thermal destruction of explosive residuals under natural settings, and to improve the design of the burn to increase the transfer of heat to the soil profile. Several recommendations are provided in the following section of this report that could form the basis for follow-up work at Eglin and/or additional range locations.

6.0 RECOMMENDATIONS FOR FUTURE EFFORTS

The data from the demonstration described in this report has shown the potential for using prescribed burning to manage explosives contamination. The further development of the FERM approach would benefit from additional laboratory and field work that incorporates the lessons learned during this investigation. The objective of the additional efforts would be to collect data that would advance the understanding of the underlying processes of thermolyses, sublimation, and melting/migration of the explosives residuals. The following recommendations are provided separately for laboratory and field work.

As a result of this effort it is clear that prescribed burning can generate sufficient heat to destroy energetic residuals at ranges. What remains to be discovered is the extent to which this process will be useful to the DOD and what may be done to optimize the process.

1. A survey should be conducted to identify ranges where prescribed burning is currently practiced. The objective would be to determine locations where current burning practice or current burning practices with minor modifications could effectively destroy energetics. A subset of the identified ranges should be selected for controlled test burning, which would be conducted under the facility's existing burn plan. Choosing ranges that have active prescribed burn programs would alleviate many of the logistical problems associated with planning an separate burn and in scheduling time to get on active ranges to setup monitoring systems and to retrieve the materials following the burn. Natural soil characterized with low mg/kg explosives residual concentrations should be identified, processed to reduce heterogeneity, and then placed back onto the ground in well marked plots. Alternatively, soil could be collected from the site, spiked to achieve low mg/kg explosives residual concentrations, and then used in the plots. The plots should be outfitted with monitoring equipment similar to that used in this SERDP investigation but include more thermocouples placed below grade. The burn should be conducted according to the facility's conventional practices unless minor modifications can be recommended that are easily implemented and that could enhance the transfer of heat into the soil. The temperature profile and the reduction in explosive residuals should be monitored as a function of temperature achieved, and over depth below the soil surface. The data collected from these burns will provide a better understanding of the benefits of current burn practices under varying range settings.
2. Phytoremediation (i.e., plant uptake) may prove to be an important mechanism for removing explosive residuals from surface soils and the residuals in and on the plant tissues would be subjected to the higher aboveground temperatures that should effectively destroy them. To gain a better understanding of the importance of this removal mechanism, follow-on work should include more extensive soil and plant sample collection and analyses at several times during the different stages of plant growth and immediately before the prescribed burn. The soils should be collected from the root zone of individual plants associated with uptake from that volume of soil (note: several plants/plant types could be associated with the same volume of soil). The sampling should target the diversity of predominant plants at the specific ranges selected for test burning. A project data set should include plant explosive residuals uptake potential for plants found at the majority of DoD ranges. This effort also should include determining the moisture and burn potential at each sampling event. This will further add to the understanding of the plant uptake and burn potential and ultimately lead to better burn

practices that take maximum advantage of plant uptake. For example, this might include more frequent rotation of target areas to allow more plant growth between burn cycles.

3. The lessons learned after implementing recommendations 1 and 2 should lead to development of a “Principles of Practice” document. This document must be developed recognizing the diverse audience to whom it should be addressed and should incorporate the following considerations.
 - a) The document needs to help environmental managers and those who do not regularly work on ranges to understand range missions and how they operate. Safety and other logistic issues associated with working on ranges and in areas where UXO and ordnance risks exist must be discussed in detail.
 - b) The document needs to include a description(s) of current DoD-range prescribed-burning practices to provide environmental managers and regulators concerned with contamination issues the level of understanding of the procedures and effects to allow them to make informed decisions on the acceptability of prescribed burning, the potential benefit of the process, and the precautions taken to insure safety and environmental protection before, during, and following the completion of the burn.
 - c) The document needs to provide detailed description of the issues associated with energetics and explosives residual contamination and the fate of those materials during burning to provide the knowledge to range operators, natural resources staff responsible for prescribed burning, regulatory personnel, and even concerned citizen groups understand the potential risks associated with live ordnance, and the potential benefits for reducing the risks associated with residuals getting into the environment.
4. Additional laboratory-based research could help optimize prescribed burning practices and lead to more effective and efficient explosives residual destruction. The following are research areas where such benefits could be realized.
 - a) Investigate plant varieties that may more effectively accumulate energetics and/or support control burns. These need to be plants that can easily and successfully be seeded in target areas, grow rapidly under the various climatic and environmental conditions at the specific ranges, and are cost effective to purchase and grow. While research has shown enhanced uptake in several plant species, targeted research on indigenous plants found on ranges is limited.
 - b) Investigate burning practices that can improve energetic destruction efficiencies. This should include investigations on the effects of soil and fuel moisture contents, supplemental fuel types and loadings, and effects of soil types and organic composition/content, optimal burning frequencies, and conditions and timing.
 - c) Conduct additional studies of the basic processes underlying thermal destruction of energetics in soil. Preliminary studies with TNT used soils from Florida (Eglin) and from New Mexico (Sandia). There was a marked difference in the TNT decomposition rate observed between the different soil types. The study was not repeated for RDX and more importantly it was not expanded to include other soil types, examining decomposition kinetics, monitoring decomposition products, and evaluating the effect of a contained atmosphere. Migration studies also should be considered to determine whether the percent sublimation and the percent of

downward migration due to melting are affected by soil type and the effect of temperature on the migration potential needs to be assessed. To better understand the factors that affect sublimation, additional studies conducted in silica and at intermediate explosive residual concentrations are needed to verify the concentration dependence.

7.0 LESSONS LEARNED DOING FIELD WORK ON AN ACTIVE RANGE

This project was undertaken on a very active range in use almost daily for critical air-to-ground combat training. Working in such an environment was necessary due to the nature of the work; however it turned out to be a very complex and challenging effort. This section is intended to convey to other researchers planning to conduct similar work, the types of issues that can be encountered. This project team consisted of several quite experienced researchers who had worked on a wide variety of military and other installations worldwide, and who believed they understood the challenges as they went into the project. The team is now older and wiser and we now recognize that this is a much more challenging environment in which to work than the average DOD field effort. We were fortunate in that the people and organizations we worked with at Eglin, without exception, were helpful and supportive and without this support the project would never have been successful. This discussion is not intended to discourage others from working on active ranges; to the contrary it is to help prepare those who want to undertake work on a range with some knowledge about the challenges.

1. You and your work is not and cannot be the most important thing happening on the range, and in most cases you will probably be the least important thing to the range's mission; get used to this and figure out how to work with it. Ranges serve a critical role in the defense establishment. Pilots need to train with specific weapons, and a wide variety of weapons need to be tested. This is not just routine training, but the lives of the pilots depend and others doing the training on it. That pilot or flight crew training on your site today could be in combat within days, their mission and safety have to be a lot more important than anything we are doing. The point is don't be surprised when you are suddenly and unexpectedly bumped from a schedule or not given access to the range. Plan for this to happen have fall-back and contingency plans. Try to schedule your work at times when the range is least likely to be needed, spend as little time on the range as possible, and be ready for the unexpected.
2. Gain an understanding of the organizational and command structure under which you will be working. Make certain that you are communicating and keeping informed all of the appropriate chains-of-command. This is not easy and there are no clear guidelines for projects like this one. Ranges and the staff that support them were not developed to support studies such as this and you will most likely be asking someone to do something that they have not done before. At Eglin, our researchers worked with several organizations, all which were necessary for the successful and safe implementation of this investigation. We worked with the base's Environmental Management (EM) offices, and Range Operations, which included additional branches and personnel for range access range safety, and range escort (EOD). In addition, our researchers worked with the Natural Resources Branch which afforded the personnel who were responsible for the design and implementation of the controlled burn.

Assume that there will be a need for multiple meetings and conference calls. A point-of-contact at the base will ultimately be one that will need to assist and interact and coordinate with all organizations and branches and with you. For our research, we worked with EM to help us identify and locate areas of interest that would support the objectives of this research. Our POC worked under the 46 Test Wing and coordinated with EM, range safety, and range control for each of the events in which we needed to access the active range to conduct the various components of our research. Our primary POC also worked with us and the lead contact at the Natural Resources Branch when the

time came to develop the controlled burn approach and to implement the burn on the range.

Be sure you understand how the range and range support personnel will be compensated for what you are doing. Range time is expensive and range support staff must be supported, many ranges operate by securing funding from those using the range. For this research, SERDP funded Eglin for the time and staff needed on range for the controlled burn. Gaining an understanding of how this will work during the planning or proposal activity, will alleviate funding and time issues later in the research.

3. Gain an understanding of EOD and safety issues; both DOD requirements and the real safety issues on site. This is critical for both you and your personal well-being and important for getting your project done. Find out when an EOD escort will be necessary, and what you can and cannot do on the range. For this project we employed our own EOD staff to assist in the development of the safety plan and Eglin supplied EOD escorts for us on site; you may have to employ your own escorts. Some examples of restrictions that were placed on our team while on the range included not being allowed to handle neat TNT; the neat material was that was used for column experiments in the field was handled by base EOD staff. It was also necessary to obtain EOD clearance before any digging, even shallow holes to place monitoring equipment. At times we had to make field changes in sampling locations at the direction of EOD staff. Digging and surface sampling activities are directed by on-site EOD as UXO and other ordnance present very real risks and the common researcher is not trained to consider or recognize these risks without trained EOD support.
4. Above all, be flexible in your plans and allow sufficient redundancy to insure that you meet your goals. We installed more of all of our sampling equipment than we needed recognizing that the site was subject to bombing during the experiment. We ended up figuring out how to do our burn in August, not the best or traditional time for controlled burning in this region. We had originally planned our burn in the spring, a better time to burn, but scheduling conflicts with the range prevented this schedule. We were lucky, as with a several day field test you can expect unscheduled missions to come up. It was certainly possible that at any time after we deployed our sampling equipment, even perhaps before or after the burn, that a mission could have come up and we would have had to wait before sampling. It was possible that our equipment and experiment could have been bombed. We did our best to keep our objectives simple and built some redundancy into our field process.

Expect for circumstances to change. The staff that you are working with may change; the mission of the range you are working on may change. For example, our project was first conceived before September 11 and before the Navy decided to close its range at Vieques. By the time the field work was scheduled, the US was at war and the Navy was moving missions to our chosen range at Eglin.

Lastly, the active range that you have characterized or become familiar with, may also change topographically due to bombing operations, blowholes and the deployment of new targets. Be prepared to improvise if necessary to accommodate your study.

8.0 REFERENCES

- Achtnich, C., P. Pfortner, M.G. Weller, R. Niessner, H. Lenke, and H.J. Knackmuss. 1999. Reductive Transformation of Bound Trinitrophenyl Residues and Free TNT During a Bioremediation Process Analyzed by Immunoassay. *Environmental Science and Technology*. 33(19):3421-3426.
- Agee, J. K. 1973. "Prescribed Fire Effects on Physical and Hydrologic Properties of Mixed-Conifer Forest Flow and Soil." University of California Water Resources Center Contribution 143.
- Bailey W. A., and M.L. Anderson. 1980. "Fire Temperatures in Grass, Shrub, and Aspen Forest Communities of Central Alberta." *Journal of Range Management*. 33(1):37-40.
- Battelle. 2003. "Impacts of Fire Ecology Range Management (FERM) on the Fate and Transport of Energetic Materials on Testing and Training Ranges". Annual Technical Report to SERDP, Compliance Program – 1305, Contract No. DACA72-02C-0038.
- Bhadra, R., D.G. Wayment, J.B. Hughes, and J.V. Shanks. 1999. Confirmation of Conjugation Process During TNT Metabolism by Axenic Plant Roots. *Environmental Science and Technology*. 33:446-452.
- Boring, L. R., J. J. Hendricks, C. A. Wilson, and R. J. Mitchell. 2004. "Season of Burn and Nutrient Losses in a Longleaf Pine Ecosystem." *International Journal of Wildland Fire*. 13(4):443-453.
- Boyle, J.J. and J.R. Shann. 1998. The Influence of Planting and Soil Characteristics on Mineralization of 2,4,5-T in Rhizosphere Soil. *Journal of Environmental Quality*. 27:704-729.
- Brooks, M. L. 2002. "Peak Fire Temperatures and Effects on Annual Plants in the Mojave Desert." *Ecological Applications*. 12(4):1088-1102.
- Carriera, L.H. and N.L. Wolfe. 1996. Isolation of a Sediment Nitroreductase, Antibody Production and Identification of Possible Plant Sources. In *IBC Symposium on Phytoremediation*, Arlington VA, May 8-10, 1996.
- Chekol, T., L.R. Vough, E.K. Dzantor, and R.L. Chaney. 2001. Plant-Soil-Contaminant Specificity Affects the Phytoremediation of TNT in Soil. In *Phytoremediation and Wetlands for Treatment of Hazardous Wastes*. (A. Leeson, E. Foote, and M.K. Banks, Eds.). Battelle Press: Columbus, OH.
- DeBano, L. F., P. H. Dunn, and C.E. Conrad. 1977. "Fires Effect on Physical and Chemical Properties of Chaparral Soils." General Technical Report WO-3. Washington, D.C., U.S. Department of Agriculture, Forest Service.
- DeBano, L. F. 1989. "Effects of Fire on Chaparral Soils in Arizona and California and Postfire Management Implications." Proceedings of the Fire and Watershed Management Symposium (N. Berg Ed.), Sacramento, CA. October 16 – 38.
- DeBano, L. F., D. G. Neary, and P. F. Ffolliott. 1998. Fire's Effects on Ecosystems. John Wiley & Sons, New York, NY.
- EPA., 1997. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods. SW-846 Update III, Office of Solid Waste, Washington, DC.

- Frandsen, W. H., and K. C. Ryan. 1986. "Soil Moisture Reduces Belowground Heat Flux and Soil Temperatures Under a Burning Fuel Pile." *Canadian Journal of Forest Research*. 16:244-48.
- Hartford, R. S., and W. H. Frandsen. 1992. "When It's Hot, It's hot... Or Maybe It's Not! (Surface Flaming May Not Portend Extensive Soil Heating)." *International Journal of Wildland Fire*. 2(3):103-44.
- Hubbard, R. M., J. M. Vose, B. D. Clinton, K. J. Elliott, and J. D. Knoepp. 2004. "Stand Restoration Burning in Oak-Pine Forests in the Southern Appalachians: Effects on Aboveground Biomass and Carbon and Nitrogen Cycling." *Forest Ecology and Management*. 190:311-21.
- Hungerford, R. D. 1989. "Modeling the Downward Heat Pulse from Fire in Soils and in Plant Tissues." Proceedings of the 10th Conference on Fire and Forest Meteorology, Ottawa, Canada. pp:148-154.
- Hungerford, R. D. M. G. Harrington, W. H. Framdsen, K. C. Ryan, and G. J. Niehoff. 1991. "Influence of Fire on Factors that Affect Site Productivity." In A.E. Harvey and L.F. Neuenschwander (Eds.) Proceeding of the Management and Productivity of Western Montane Forest Soils. USDA Forest Service, Intermountain Research Station, General Technical Report INT-280.
- Hughes, J.B., J.V. Shanks, M. Vanderford, J. Lauritzen, and R. Bhadra. 1997. Transformation of TNT by Aquatic Plants and Plant Tissue Cultures. *Environmental Science and Technology*. 31:266-271.
- Hughes, J.B., C.Y. Wang, R. Bhadra, and A. Richardson. 1998. Reduction of 2,4,6-Trinitortoluene by *Clostridium acetobutylicum* through Hydroxylamino-Nitrotoluene Intermediates. *Environmental Toxicology Chemistry*. 17:343-348.
- Jenkins, T. F., M. Walsh, P. Thorne, P. Miyares, T. Ranney, C. Grant, and J. Esparza. 1998. *Site Characterization for Explosives Contamination at a Military Firing Range Impact Area*. U.S. Army Cold Regions Research and Engineering Laboratory, Special Report 98-9.
- Jenkins, T. F., P. H. Miyares, N. H. Collins, A. D Hewitt.; T. A. Ranney. 2000a. *Use of Surface Snow Sampling to Estimate the Quantity of Explosives Residues Resulting from Landmine Detonations*. ERDC Technical Report.
- Just, C. L. and J. L. Schnoor. 2004. "Phytophotolysis of Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) in leaves of Reed Canary Grass." *Environmental Science & Technology*. 38(1):290-295.
- Kremens, R.; Faulring, J.; Hardy, C. 2003b. Measurement of the Time-Temperature and Emissivity History of the Burn Scar for Remote Sensing Applications. 2nd International Wildland Fire Ecology and Fire Management Congress, 16-20 November, Orlando FL. American Meteorological Society.
- Larson S. L., Strong A. B., Yost S. L., Escalon B. L, and Parker D. 1998. *Analysis of Explosives in Plant Tissues: Modifications to Method 8330 for Soil*. USACE, Waterways Experiment Station. Technical Report IRRP-98-5.
- Larson, S.L., R.P. Jones, L. Escalon, and D. Parker. 1999. Classification of Explosives Transformation Products in Plant Tissue. *Environmental Toxicology Chemistry*. 18:1270-1276.

- Massman, W. J., J. M. Frank, W. D. Shepperd, and M. J. Platten. 2003. *In Situ Soil Temperature and Heat Flux Measurements During Controlled Surface Burns at a Southern Colorado Forest Site*. USDA Forest Service Proceedings RMRS-P-29. pp. 69 – 87.
- Medina, V.F., S.C. McCutcheon, N.L. Wolfe, and S.L. Larson. 1997. Phytoremediation of Explosives in Soil and Water: Engineering Studies. Fourth International In Situ and On-Site Bioremediation Symposium. 3:301. Battelle Press: Columbus, OH.
- Molina, M. J., and J. V. Llinares. 2001. "Temperature-Time Curves at the Soil Surface in Marquis Summer Fires." *International Journal of Wildland Fire*. 10(1):45-52
- Neary D. G., C. C. Klopatek, and L. F. DeBano, and P. F. Ffolliott. 1999. "Fire Effects on Belowground Sustainability: A Review and Synthesis." *Forest Ecology and Management*. 122:51-71.
- Neary, D. G. 2004. "Fire Effects on Soils." *Southwest Hydrology*. pp. 18-19.
- Oxley, J. C., A. Kooh, R. Szeckeres, and W. Zheng. 1994a. "Mechanisms of Nitramines Thermolysis" *Journal of Physics Chemistry*. 98:7004-7008.
- Oxley, J. C., J. L. Smith, and E. Resende. 2003. "Pearce, E "Quantification and Aging of the Post-Blast Residue of TNT Landmines." *Journal of Forensic Science*. 48(4)
- Oxley, J. C., J. L. Smith, and W. Wang. 1994b. "Compatibility of Ammonium Nitrate with Monomolecular Explosives, Part I." *Journal of Physics Chemistry*. 98: 3893-3900. Part II. *ibid* 3901-3907.
- Oxley, J. C., J. L. Smith, H. Ye, R. L. McKenney, and P.R. Bolduc. 1995. "Thermal Stability Studies on Homologous Series of Nitroarenes." *Journal of Physics Chemistry*. 99(24):9593-9602.
- Pennington, J. C. Environ. Lab., Army Engineering Waterway Experiment Station., Vicksburg, MS, USA. Avail. NTIS. Report (1988), (WES/TRIEL-88-12; Order No. AD-A200502), 183 pp. From: Gov. Rep. Announce. Index (U. S.) 1989, 89(5), Abstr. No. 911,378.
- Pennington, J.C. 1998. *Plant Uptake of 2,4,6-Trinitrotoluene, 4-Amino-2,6-Dinitrotoluene, and 2-Amino-4,6-Dinitrotoluene Using 14C-Labeled and Unlabeled Compounds*. Technical Report EL-88-20, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi.
- Raison, R. J., P. V. Woods, B. F. Jakobsen, and G. A. V. Bary. 1986. "Soil Temperatures During and Following Low-Intensity Prescribed Burning in a *Eucalyptus pauciflora* Forest." *Australian Journal of Soil Research*. 24(1):33-47.
- Ryan, K. C., and W. H. Frandsen. 1991. "Basal Injury from Smoldering Fires in Mature *Pinus ponderosa* Laws." *International Journal of Wildland Fire*. 192):107-118.
- Schneider, J.F., N.A. Tomczyk, S.D. Zellmer, and W.L. Banwart. 1994. *Uptake of Explosives from Contaminated Soil and Existing Vegetation at the Joliet Army Ammunition Plant*. Technical Report ANL/ESD/TM-65, Argonne National Laboratory, Argonne, IL.
- Schneider J.F., S.D. Zellmer, N.A. Tomczyk, J.R. Rastorfeer, D. Chen, and W.L. Banwart. 1995. *Uptake of Explosives from Contaminated Soil by Existing Vegetation at the Iowa Army Ammunition Plant*. Technical Report SFIM-AEC-ET-CR-95013.

- Smith, A. M. S., M. J. Wooster, N. A. Drake, F. M. Dipotso, M. J. Falkowski, and A. T. Hudak. 2005. "Testing the Potential of Multi-Spectral Remote Sensing for Retrospectively Estimating Fire Severity in African Savannahs." *Remote Sensing of Environment*. 97(2005):92-115.
- Valette, J. C., V. Gomendy, J. Marechal, C. Houssard, and D. Gillon. 1994. "Heat Transfer in Soil During Very Low-Intensity Experimental Fires: The Role of Duff and Soil Moisture Content." *International Journal of Wildland Fire*. 4(4):225-37.
- Vanderford, M., J.V. Shanks and J.B. Hughes. 1997. Phytotransformation of Trinitrotoluene (TNT) and Distribution of Metabolic Products in *Myriophyllum aquaticum*. *Biotechnology Letters*. 19:277-280.
- Walsh, M. E., C. A. Ramsey, and T. F. Jenkins. 2002. "The Effect of Particle Size Reduction by Grinding on Subsampling Variance for Explosive Residues in Soil." *Chemosphere*. 49:1267-1273.
- Wang, C. and J.B. Hughes. 2001. Phytotransformation of TNT in *Myriophyllum aquaticum*: A Complex Pathway through Hydroxylamino Intermediates. In *Phytoremediation and Wetlands for Treatment of Hazardous Wastes*. (A. Leeson, E. Foote, and M.K. Banks, Eds.). Battelle Press: Columbus, OH.
- Wang, C.Y., D. Zheng, and J.B. Hughes. 2000. Stability of Hydroxylamino and Amino Intermediates from Reduction of 2,4,6-Trinitrotoluene, 2,4- and 2,6-Dinitrotoluenes. *Biotechnology Letters*. 22:15-19.